TECHNISCHE UNIVERSITÄT MÜNCHEN
Lehrstuhl für Anorganische Chemie

Synthesis, Immobilization, and Applications of Solvent Stabilized Transition Metal Cations with Weakly Coordinating Anions

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Vollständiger Abdruck der von der Fakultät für Chemie der Technischen Universität München zur Erlangung des akademischen Grades eines

Doktors der Naturwissenschaften

genehmigten Dissertation.

Vorsitzender: Univ.-Prof. Dr. J. P. Plank

Prüfer der Dissertation: 1. Univ.-Prof. Dr. F. E. Kühn

2. Univ.-Prof. Dr. K.-O. Hinrichsen

Die Dissertation wurde am 25.06.2008 bei der Technischen Universität München eingereicht und durch die Fakultät für Chemie am 29.07.2008 angenommen.

Die vorliegende Arbeit enstand in der Zeit von September 2005 bis Juni 2008
am Anorganische-chemischen Institute der Technischen Universität München

I would like to express my deep gratitude to my academic supervisor

Univ.-Prof. Dr. Fritz E. Kühn

for giving me the opportunity to work in his laboratory, his continuous supervision, encouragement and confidence in me and my work

Diese Arbeit wurde durch die BASF AG (The Chemical Company) gefördert

To my father, my mother,
my family
and all my friends
with deep gratitude and love

Acknowledgments

I would like to start by expressing my obedience, thankfulness and gratitude to ALLAH, from whom I always receive protection guidance and help.

My thanks and great gratitude goes to my academic supervisor, Prof. Fritz E. Kühn for giving me the opportunity to work in his group, for his superior supervision, encouragement, constructive comments and trust in me and in my work.

I would also to express my gratitude to Dr. Ahmed Hijazi for introducing me into the field of my study and his help in the beginning of my work. To Dr. Ayyamperumal Sakthivel, Dr. Jin Zhao, Dr. Filipe Pedro and Dr. Syukri, I am very grateful for them. Prof. Brigitte Voit, Dr. Hans-Michael Walter, Dr. Phllip Hanefeld and Dr. Narayanan Krishnan are acknowledged for the excellent cooperation in the field of polymerization of olefins.

All the thanks to Dr. Eberhardt Herdtweck for the X-ray structural determination included in this thesis. I am also thankful to Ms. Ammari and her co-workers for the elemental analysis, to Mrs. Georgeta Krutsch for the assistance in the NMR and the TG-MS measurements and for also being kind all the time.

Special thanks for Prof. Ahmad M. Al-Ajlouni (Jordan) and his family, Prof. Ying Zheng (Canada), Prof. Özgül Saglam (Turkey) and Dr. Mei Zhang-Presse (China) for their kindness and support.

Mrs. Grötsch, Mrs. Kaufmann, Mrs. Schuhbauer from the secretary's office are acknowledged for their help with organization and burocratic matters.

To all my colleagues: Alejandro Capape Miralle, Mingdong Zhou, Yang Li, Kavita R. Jain, Alev Günyar, Bernd Diebl, Alexander Raith, Silvana Rach, Christian Fischer, Nadezda Domanovic and Serena Goh all the thanks for the nice working atmosphere in the laboratory and for their friendship in the normal life.

I would like to thank my friends in Munich, Abdel Hakeem Hassabou and his family, Mohammad Herz-Allah and his family, Dr. Haytham Rashidi and his wife, Mahmoud Mahgoub, Mahmoud Kayari (abu Alnoor), Dr. Amjad Basha (India), Ahmad Habbaba, Qutaiba abu Salem (Tübingen), Tareq Alshbool (Jena) and Dr. Fares Kairallah (Italy) for being so helpful and very close friends to me

BASF AG (The Chemical Company) is acknowledged for the financial support for my Ph.D work.

Finally I would like to give my special and heartfelt gratitude thanks to my family in Jordan, to my mother and father for their endless love and support, to my brother and sisters, to all my friends in Jordan.

Abbreviations

BET	Brunauer-Emmett-Teller
Brij-30	1,3-diacetoxy-1,1,3,3-tetrabutyltin oxide polyethelene glycol dodecyl ether
Calcd.	Calculated
Cat.	Catalyst
CPMAS	Cross Polarization Magic Angle Spinning
CTABr	Hexadecyltrimethyl Ammonium Bromide
EA	Elemental Analysis
EDA	Ethyldiazoacetate
e.g.	for example
EPR	Electron Paramagnetic Resonance
FT-IR	Fourier Transform Infrared
GC-MS	Gas Chromatography coupled with Mass Spectroscopy
Fig.	Figure
M	Metal
MCM	Mobile Crystalline Material
Me	Methyl
M_n	Average Molecular Weight
NMR	Nuclear Magnetic Resonance
PDI	Polydispersity Index
P4VP	Poly(4-vinylpyridine)
Resp.	Respectively
ROMP	Ring Opening Metathesis Polymerization
RT	room temperature
TEM	Transmission Electron Microscopy
TFPB	Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate

TGA	Thermogravimetric Analysis
TG-MS	Thermogravimetry coupled with Mass Spectroscopy
THF	Tetrahydrofuran
TMAOH	Tetramethyl Ammonium Hydroxide
VP	Pore Volume
WCA	Weakly Coordinating Anion
XAFS	X-ray Absorption Fine Structure
XRD	X-ray Diffraction
ν	wave number (cm^{-1})

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1. Introduction

Since their discovery 150 years ago,[1] a large number of transition metal organonitrile complexes have been synthesized and found valuable applications. In most cases, the usefulness of these complexes results from the labile coordination mode of the nitrile ligands, which can be easily replaced by more strongly coordinating ligands[2, 3] thus making the complexes suitable starting materials for the synthesis of other complexes,[4, 5] inorganic materials [6, 7] and catalysts.[8] The preparation and synthetic application of acetonitrile complexes of the type $[M^{II}(NCCH_3)_6][X]_2$ (M = Mn and Cu and X = BF_4^-, $B(C_6F_5)_4$ and $B\{C_6H_3(m\text{-}CF_3)_2\}_4^-$) were achieved. They have found to be catalytically active towards polymerization of isobutene, cyclopropanation of olefins, olefins aziridination and aldehyde olefination reactions[2, 6, 9, 10]

1.1. Weakly coordinating anions (WCAs)

The term "non-coordinating anion" was first coined to describe anions such as ClO_4^-, $SO_3CF_3^-$, SO_3F^-, BF_4^-, PF_6^-, AsF_6^- and SbF_6^-, which were found to be non-coordinating in aqueous solutions, [11] X-ray crystallography proved that in most cases these anions can be easily coordinated.[12, 13] However with the advent of routine X-ray crystallography it has become evident that in many cases a "non-coordinating" complex anion can in fact easily coordinate. Accordingly, the term weakly coordinating anion (WCA) was coined for the coordination of these complex anions.

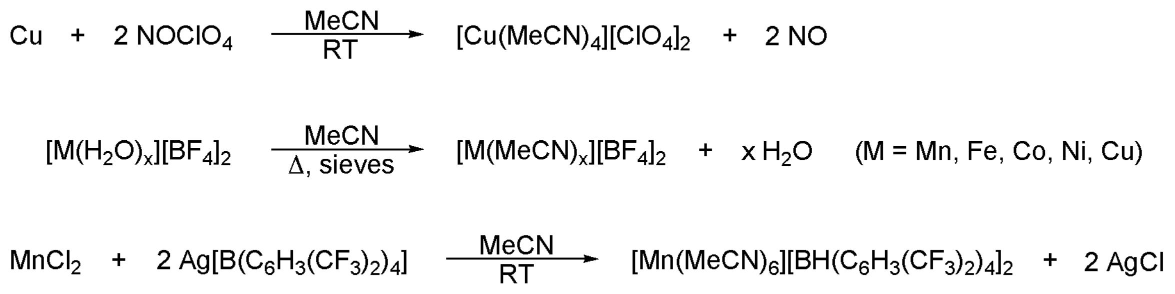
As a result of their capability in enhancing the reactivity of metal complexes, the use of weakly or non-coordinating anions as counter anions is of significant interest in both synthesis and catalysis [11, 12, 14] Owing to the importance of such WCAs in fundamental and applied chemistry, a considerable amount of work has been undertaken in order to obtain more examples of these interesting anions.

In the last three decades, a plethora of species that closely resemble non-coordinating anions has been synthesised. In order to produce a more weakly coordinating anion, the negative charge was delocalized over a large area of non-nucleophilic and chemically robust moieties. Several approaches to achieve this goal have been used: Exchange of the fluorine atoms in $[BF_4]^-$ ions for phenyl groups leads to the long known larger $[BAr^F{}_4]^-$ ions (Ar^F = $-C_6F_5$, [15] $–C_6H_3$-3,5-$(CF_3)_2$,[16]… etc). Anions such as $[CB_{11}H_{12}]^-$ can be synthesized from $NaBH_4$, $CHCl_3$, base, and $BF_3{\cdot}OEt_2$.[16] Oxophilic and strongly Lewis acidic atoms M (M = B^{III}, Al^{III}, Nb^{V}, Ta^{V}, Y^{III}, La^{III}, etc) as centre with poly- or perfluorinated alkoxy- (OR^F) and aryloxy- (OAr^F) formed complexes $[M(OR^F)_n]^-$ [17] and $[M(OAr^F)_n]^-$ [18] $[MF_6]^-$ (M = As, Sb) was also formed by reaction with Lewis acid.[19, 20] Examples for other quite weakly coordinating anions are BPh_4^-, $CB_{11}H_{12}^-$ and related carborane anions, $OTeF_5^-$ and its derivatives, polyoxoanions such as $PW_{12}O_{40}^{3-}$, $HC(SO_2CF_3)_2^-$ and related anions, C_{60}^-, $B(o\text{-}C_6H_4O_2)_2^-$, anionic methylalumoxanes (MAO), and H(1,8-$C_{10}H_6(BMe_2)_2)^-$ (hydride sponge).[11]

There are several common strategies to introduce a WCA into a system. Silver salts of WCAs may oxidize the transition metal complexes of moderate oxidation potential and transition-metal salts of WCAs are formed at the same time.[21] The replacement of methyl-groups from $[Cp_2M(CH_3)_x]$ (M = Ti, Zr, Hf, Ta; x = 2, 3) by strong organometalic Lewis acids like $B(C_6F_5)_3$ produces the tight ion pair $[Cp_2MMe^+][MeB(C_6F_5)_3^-]$.[22] WCAs can also be introduced into a system through metathesis reactions of $M^+[X]^-$ ($[X]^-$ = WCA, M = univalent metal, such as Li, Na, K, Ag, Tl) with weak or sometimes even covalently bonded halides. In many cases, Ag^+ is the best cation to abstract the halide from the substrate. Silver salt metathesis is a time-honoured method of halide ion abstraction. Its origin dates back to the early days of coordination chemistry. Silver nitrate was already established as the standard testing reagent to differentiate between free and complexed chloride. Recently, the availability of numerous silver salts of WCAs, AgY (Y = ClO_4^-, SbF_6^- etc), have exceeded silver salt metathesis as the widely used method of halide ion abstraction. In general, a weakly coordinating anion can be produced by delocalizing the negative charge over a large area of non nucleophilic and chemically robust moieties. However, one should still bear in mind that the coordinating ability of each anion is limited by its most basic site. That is, just like a chain breaks with its weakest link, a WCA will always (albeit weakly) coordinate with its most nucleophilic, sterically accessible moiety, which may be the starting point for anion decomposition. The art of constructing the "ultimate non coordinating anion" is therefore to realize a structure without an accessible basic site. This may be achieved by a combination of steric and electronic effects.

1.2. Synthesis and general overview of acetonitrile ligated metal(II) complexes:

First row transition metal complexes of general formula $[M(NCCH_3)_6][A]_2$ (M^{II} = Cr, Mn, Fe, Co, Ni, Cu, Zn; A = counter ion) and some of their dimeric second and third row congeners of formula $[M_2(NCCH_3)_{8-10}][A]_2$ (M^{II} = Mo, Tc, Re, Rh; A = counter ion) have been known for several years.[23] Several groups have contributed to their synthesis. Generally they can be synthesized by several methods. One of them is the oxidation of metals with nitrosonium salts of the intended counter anion,[24] another possibility is the dehydration of aqueous salts.[25] Further synthetic options exist,[26] but the common method to introduce WCAs to the organonitrile complexes is by metathesis reagents such as silver salts, potassium salts and amine salts (see scheme 1.1) to introduce anions (WCAs) to the organonitrile complexes.[27-31]



Scheme 1.1: Methods for the preparation of organonitrile complexes with weakly coordinating anions.[25, 32-34]

Another is through the reaction of metal halides with BCl_3, $AlCl_3$, $GaCl_3$, $InCl_3$, $TlCl_3$ and $FeCl_4$, resp. to form complexes of general formula $M(NCMe)_{np}^{+}(M' Cl4)_{p}^{-}$.[35-38] All the reactions were carried out in nitrile solvents.

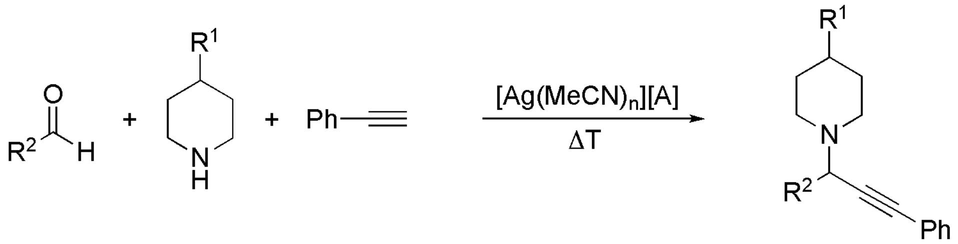
1.3. Applications of solvent ligated complexes with weakly coordinating anions

Solvent coordinated monomeric transition metal(II) complexes have been known for a long time.[2, 5, 14, 39-43] These complexes are synthetically important. The successful synthesis of a series of acetonitrile complexes of the type $[Mn(NCCH_3)_6][X]_2$ where X = BF_4, $B(C_6F_5)_4$, $B\{C_6H_3(m\text{-}CF_3)_2\}_4$, $((C_6F_5)_3B–\ C_3H_3N_2–B(C_6F_5)_3)$, exhibiting excellent activities for the polymerization of cyclopentadiene, methylcyclopentadiene and isobutene, in homogeneous and heterogeneous phase has been reported. [44-50]

A range of dimeric solvent stabilized transition metal complexes with the metal atoms in the formal oxidation state + II such as $[Mo_2(NCCH_3)_{8\text{-}10}][X]_4$ where X = BF_4 have been synthesized during the last decade.[2, 3, 7] They are widely regarded as useful starting materials in synthetic chemistry since their weakly coordinating solvent ligands, e. g. acetonitrile and tetrahydrofuran (THF) can be easily replaced by more strongly coordinating ligands.[6, 51, 52] In this way, they have also been applied as building blocks for inorganic and organometallic macromolecules,[6, 9, 10, 53] However, because of their high reactivity many side reactions may occur, with consequent limitation of their synthetic potential.[54] Recently, the application of dimeric transition metal (II) complexes stabilized by solvent molecules as initiators in homogeneous and heterogeneous polymerization reactions has been attracting interest. [55-58]

1.3.1. Catalytic activity of monomeric metal (II) complexes

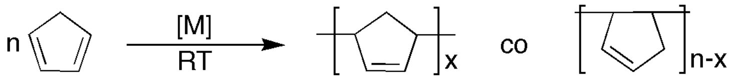
Complexes of general formula $[M(NCCH_3)_{2-6}][A]_{1-2}$ have found many applications. $[Cu(NCCH_3)_4][A]$ (A = BF_4, PF_6, ClO_4, etc) are good catalysts and good precursors of asymmetric catalysis of 1, 4-addition of diethylzinc to α, β-unsaturated enones, aza Diels-Alder reactions of N-sulfonyl imines, [2 + 2] cycloaddtion of 1-methoxyallenylsilane with α-imino ester, Mannich-type reactions, alkene aziridination etc..[57] $[Ag(MeCN)_4][A]$ (A = BF_4, ClO_4) can be used as starting materials for the synthesis of cubic clusters,[56, 58] luminescent heterometallic materials[59], coordination polymers[60] and the synthesis of other transition metal complexes.[61] The complexes $[Ag(MeCN)_4][A]$ (A = $B(C_6F_5)_4$, $(C_6F_5)_3B\text{-}C_3H_3N_2\text{-}B(C_6F_5)_3$) and $[Ag(MeCN)_2][B(C_6H_3(CF_3)_2)_4]$ show catalytic activity in coupling reactions of terminal alkynes with aldehydes and amines, generating three-component propargylamines (see scheme 1.2).[61, 62]



Scheme 1.2: Coupling of phenylacetylene with an aldehyde (R^2 = aryl) and a dialkylamine (R^1 = H, Me) catalysed by silver(I) complexes (n = 2:.A = $B(C_6H_3(CF_3)_2)_4$; n = 4: A = $B(C_6F_5)_4$, $(C_6F_5)_3B\text{-}C_3H_3N_2\text{-}B(C_6F_5)_3$).[62]

Complexes of general formula $[M(NCCH_3)_{2-6}][A]_{1-2}$ can be used as initiators in the cationic polymerization of cyclopentadiene and methylcyclopentadiene in both homogeneous and heterogeneous phase.[63] In this case $[BF_4^-]$ was applied as a counter anion and the Mn(II) complex turned out to be the most active initiator . In general complexes of general formula $[M(NCCH_3)_{4-6}][A]_{1-2}$ have not only found application in different fields of chemistry, but are also quit easy to synthesize.

It has been demonstrated that solvent coordinated monomeric Complexes of the type $[M(MeCN)_n][(BF_4)]_2$ (M = Pd^{II} or first row transition metal ions, n = 4,6) (see chart 1.1) exhibit high activities as initiators for cationic (methyl)cyclopentadiene polymerization in homogenous phase (see scheme 1.3).[42]



Scheme 1.3: Polymerization of cyclopentadiene.

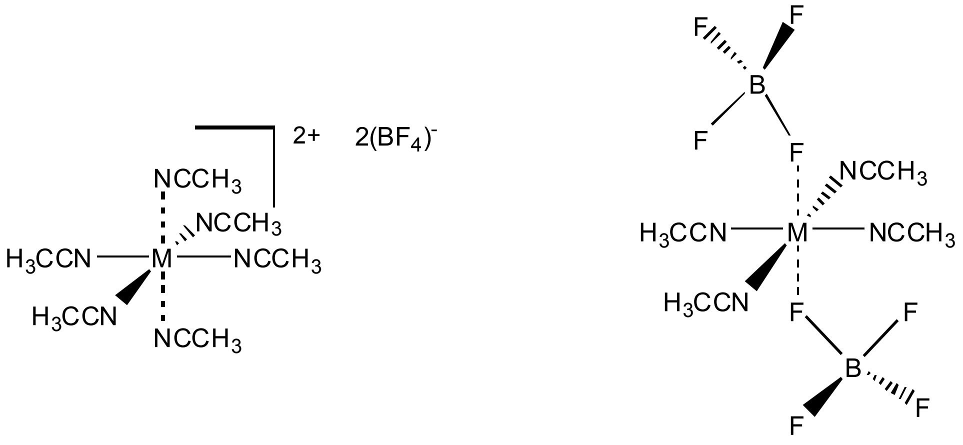
The highest polymer yields in the polymerization of cyclopentadiene are obtained with M = Cr, Mn, Fe and Zn, analogous V and Ni complexes are nearly or completely inactive (see table 1.1).[42]

Table 1.1: Cyclopentadiene polymerization

Catalyst	c_i^a (mol/L)	PY^b (%)
$[Mn(MeCN)_4][(BF_4)]_2$	0.000625	100
$[Zn(MeCN)_4][(BF_4)]_2$	0.00125	100
$[Fe(MeCN)_4][(BF_4)]_2$	0.00125	94
$[Cr(MeCN)_4][(BF_4)]_2$	0.00125	92
$[Ni(MeCN)_4][(BF_4)]_2$	0.00125	15
$[V(MeCN)_6][(BF_4)]_2$	0.00125	0

(t = 16 h, T = 25 °C, solvent = methylene chloride, C_0(cyclopentadiene) = 2.27 mol/L).

^{a} = concentration of the initiator. ^{b} = polymer yield.



M = V(II)

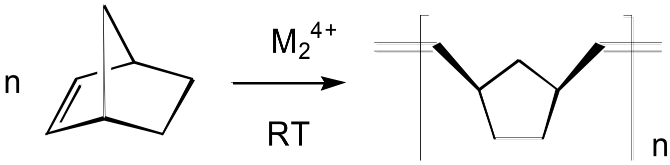
M = Cr(II), Mn(II), Fe(II), Co(II), Ni(II), Pd(II), Cu(II), Zn(II)

Chart 1.1

In general, the observed activity of the monomeric complexes correlates well with the ligand field stabilization energy as a function of the number of d electrons for octahedrally coordinated transition metals in the formal oxidation state +II. The lower the stabilization energy of the complexes, the higher is their activity as initiators. This observation again supports the idea that the mechanism proceeds via coordination of a substrate molecule to the metal centre by replacement of the weakly coordinating solvent ligand. The counter ions have a pronounced influence on the catalytic performance. Non coordinating anions can significantly improve the activity of the cations. The reaction temperature seems to be of the significant importance: above 50 ºC, the complex activity declines, possibly due to complex decomposition or competitive inhibition by dicyclopentadiene.

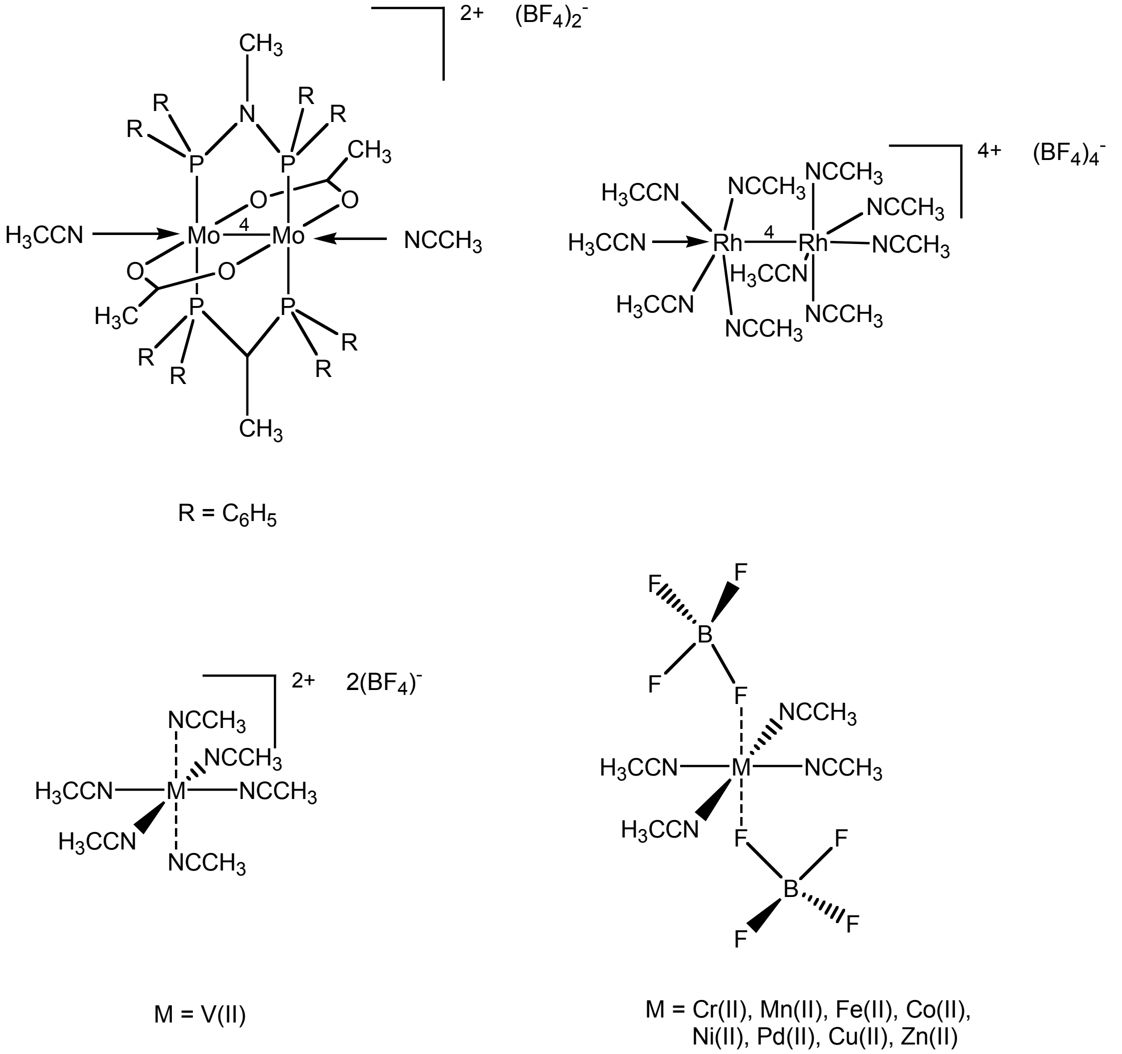
1.3.2. Catalytic activity of dimeric metal (II) complexes

Dianionic dimolybdenum(II,II) salts $[NEt_4]_2[Mo_2(\mu\text{-}O_2CMe)_2Br_4]$ (**1**) and the dicationic dimolybdenum(II,II) salts $[Mo_2(\mu\text{-}O_2CR)_2(MeCN)_n][BF_4]_2$ (R = Me, n = 6 (**2**); R = $CMeCH_2$, n = 4 (**3**)) and $[Mo_2(MeCN)_8][BF_4]_4$ (**4**) are efficient catalysts for the room temperature ring-opening metathesis polymerization (ROMP) of norbornene (bicyclo[2.2.1]hept-2-ene) in the presence of $AlEtCl_2$ as a cocatalyst (Scheme 1.4).[64, 65] The polymerization activity can be attributed to the lability of the acetonitrile ligands.[66] ^1H and ^{13}C NMR studies of the complex **2** have shown that, at room temperature, both the axial and equatorial acetonitrile molecules undergo rapid exchange with CD_3CN.[67]



Scheme 1.4. Ring-opening metathesis polymerization of norbornene

Recently, it has been shown that a broader variety of dimolybdenum complexes exhibit activities as initiators in cationic polymerization reactions (see Chart 1.2).[41] Both the cation charge and the effective charge at the metal center play a crucial role for the initiator activity. If all other parameters are constant, it has been shown that electron-withdrawing ligands improve, while electron-donating ligands reduce the initiator activity of the complexes. An increase of initiator concentration leads to an increase of the amount of product, to an increase of the polydispersity index (PDI) and to a decrease of the number average of the molecular weight.



R = C_6H_5

M = V(II)

M = Cr(II), Mn(II), Fe(II), Co(II), Ni(II), Pd(II), Cu(II), Zn(II)

Chart 1.2. Dimeric and monomeric metal(II) complexes.

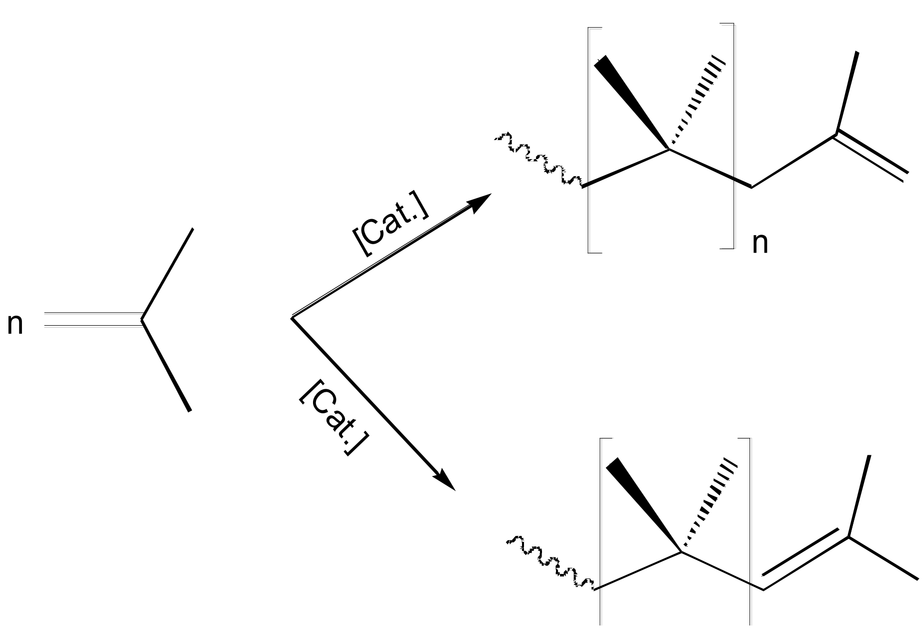
1.4. Previous catalytic results on isobutene polymerization, olefination and cyclopropanation

1.4.1. Polymerization reaction of isobutene

It is well established that isobutene can be polymerized by means of cationic initiators such as protons or Lewis acids. Typical catalysts are $AlCl_3$, BCl_3, BF_3 and water as co-initiator. Typical solvents are methylchloride, dichloromethane and ethene at temperatures of -80 °C or below (-100 °C in case of ethene as solvent). Polymerization under these conditions, however, is extremely fast and exothermic. BF_3 combined with aliphatic alcohols as deactivators is applied for the production of highly reactive polyisobutene. Reaction temperatures of – 30 °C up to 0 °C are commonly used for this process.

Polyisobutenes in general (scheme 1.5), can be divided in three large groups according to their molecular weight, having different properties and usage. High-molecular polyisobutenes with a molecular weight of at least 120 kg/mol are rubber-like polymers and are used for example in un-crosslinked rubber goods and as a chewing gum base. They are generally produced with Lewis acid initiators and traces of water at very low temperatures significantly below -80°C[68]. Medium molecular weight polyisobutenes with a molecular weight between 40 and 120 kg/mol are highly viscous liquids, mainly used as glues and sealing compounds [68, 69]. Low-molecular weight polyisobutenes have molecular weights of 0.3 – 3 kg/mol and are viscous, honey-like liquids. They are available by means of Lewis acidic initiators, e. g. aluminium alkyl chlorides or aluminium(III) chloride[68, 69]. Usually, polyisobutenes prepared in this way contain less than 10 % terminal double bonds and display a polydispersity index between 2 and 5.

The so-called highly reactive polyisobutenes differ from these conventional polyisobutenes. They contain a high percentage of terminal double bonds (> than 60%). These polymers are used in several applications, such as intermediates in the preparation of additives for lubricants and fuels[70]. In functionalization reactions, the terminal double bonds play a very important role, and therefore, a high number of terminal double bonds are an important quality criterion for these polyisobutenes.

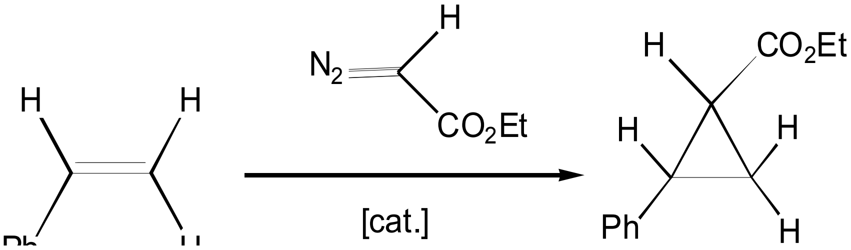


Scheme 1.5. Polymerization of isobutene.

Adjustable medium molecular weights of 0.5-5 kg/mol and molecular weight distributions are also of importance for the industrial application of the highly reactive polyisobutenes. Several synthetic strategies towards the desired products have been described and patented. They focus mainly on the use of chloride-free, Lewis-acid based initiators like BF_3 for polymerization or aluminium(III)chloride as initiators with an additional step of dehydrochlorination of the chloride terminated polyisobutenes obtained in this way[71-74]. In all cases the products can only be obtained in good yields and with a percentage of the desired terminal double bonds higher than 80% at reaction temperatures significantly below 0 °C. However, performing the reaction at such low temperatures incurs considerable costs, very much reducing the economy of the process.

1.4.2. Cyclopropanation reaction

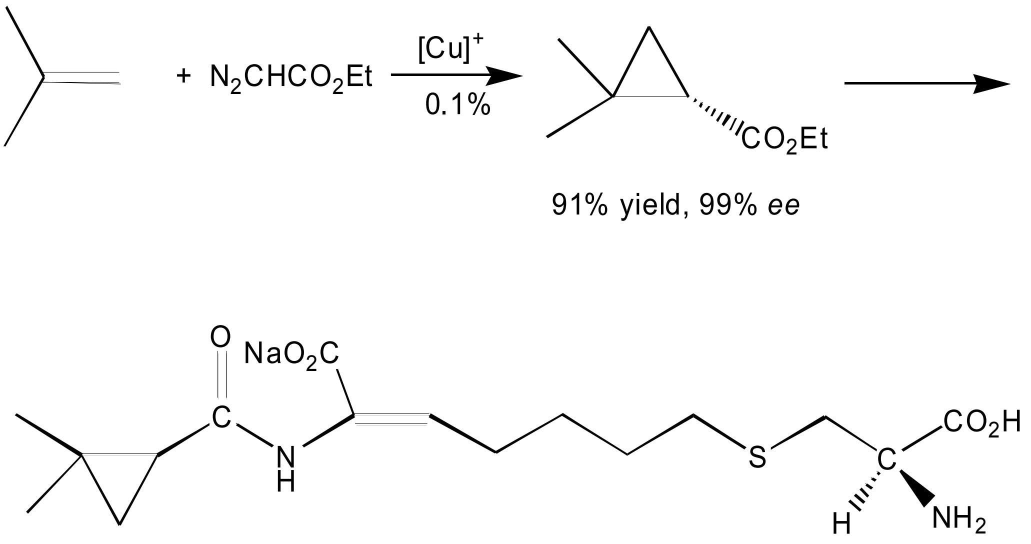
The use of complexes with weakly coordinated, easily displaceable ligands, should - in principle - have a positive effect on the catalytic activity, by rendering the intermediate species more accessible to substrate coordination. The negative effect of excess ligand in cyclopropanation catalysis with metal complexes has been observed previously.[75, 76] These complexes were tested as catalysts for cyclopropanation reactions using styrene as olefin (Scheme 1.6).



Scheme 1.6. Styrene cyclopropanation.

The influence of the styrene:ethyldiazoacetate (EDA) ratio on the reaction yield was studied.[75, 76] 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. In all the reactions of EDA with an excess of olefin in the presence of metal complexes to give corresponding cyclopropanes, fumaric acid esters were detected as by-products, but no by-products containing styrene were found.[75-78]

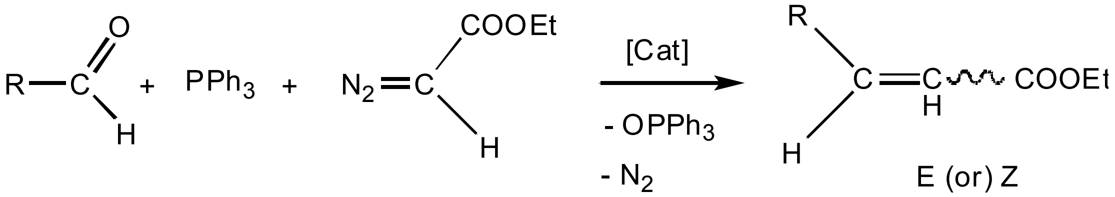
Several mechanistic studies on catalytic cyclopropanation reactions have been performed recently.[79, 80] It is generally accepted that transition metal catalyzed cyclopropanation reactions involve the existence of a metal-carbene complex, formed by association of the diazo compound with the catalyst under liberation of N_2. For example, the formation of the copper-carbene intermediate was shown to be the rate-determining step of the cyclopropanation reaction.[81, 82] The cyclopropanations were initially carried out with copper(II) chiral Schiff base and later with semicorrin Cu(II) complexes. The actual catalysts are however Cu(I) species, which suggested the direct use of Cu(I) complexes as catalyst precursors. Chiral semicorrin-copper complexes are efficient enantiomeric catalysts for intramolecular cyclopropanation reactions of diazomethyl alkenyl ketones leading to bicyclohexan-2-ones with up to 85% *ee* and to bicycloheptan-2-ones with up to 95% *ee*.[83] Practical applications include the synthesis of 2,2-dimethylcyclopropane carboxylate from isobutene, a key step in the commercial production of cilastatin (scheme 1.7.). Cilastatin is a dehydropeptidase which acts as an *in vivo* stabilizer of the carbapenem antibiotic imipenem with achiral diazoesters.



Scheme 1.7.

1.4.3 Olefination reactions

The olefination of aldehydes is an important transformation in organic synthesis as the formation of a carbon-carbon double bond is one of the most convenient and universal methods for the preparation of alkenes. Although the Wittig reaction and its modifications [84-86] are highly effective and commonly used methods, there are still several drawbacks such as the low selectivity for some ylides, the possible epimerization of base-sensitive substrates and the involvement of multi-step processes.[87-91] Some of the reaction systems employ stoichiometric organometallic reagents, such as titanium and zinc based reagents. However, the use of stoichiometric amounts of metal containing systems is an undesired factor indicating that there is still a significant need to develop better reagents to carry out Wittig type reactions. A particularly favourable way to improve or enable aldehyde olefination reactions is to treat organometallic reagents as catalysts (Scheme 1.8.).[92]



Scheme 1.8. General equation for the aldehyde olefination reaction

Huang et al. presented a reaction of tributylstibine, diazocompounds, carbonyl compounds (including both aldehydes and ketones) and a catalytic amount of Cu^{I}I, and the olefin yields reached 98 % within 4 hours at reaction temperatures between 40 – 80 °C. 5–20 mol % catalyst has been used for this transformation. Stibonium ylides are formed as intermediates. Several Cu containing compounds representing Cu oxidation states between 0 and 2 have been examined. The most efficient catalyst was found to be Cu^{I}I [93] In a continuation of this work, Huang et al. demonstrated that a reaction of diorganyl telluride, diazocompounds and carbonyl compounds (including again both aldehydes and ketones) and a catalytic amount of Cu^{I}I improves the yields of olefination products up to 95 % while other Cu complexes produce lower yields.[94] 30 mol % of the CuI complex is consumed in this reaction. Shastin et al. serially reported on a related catalytic olefination reaction of aromatic aldehydes and ketones.[95-100] they reported that N-unsubstituted hydrazones of aromatic carbonyl compounds can be transformed into the corresponding substituted alkenes by treatment with polyhalogenated alkanes in the presence of catalytic amounts (10 mol %) of CuCl. Here, Cu(I) is oxidized to Cu(II), which is then used in the production of the alkenes.

Recently, Ruthenium(II) salen complexes have also been reported to be efficient as catalysts in the olefination of various aldehydes in homogeneous phase.[101] Their high catalytic activity is probably due to the flexibility of the ethylenediamine backbone of the salen ligands as described for a number of transition metal complexes with bidentate oxygen ligands.[102] However, there is a drawback for this homogeneous reaction system; the formation of μ-oxo dimers and other polymeric species, which leads to irreversible catalyst deactivation. In principle, this problem can be solved by isolating the metal-salen complexes from each other by encapsulating them in the cavities of molecular sieves. This approach can slow down the degradation of the complexes.[103-105] Furthermore, the porosity of mesoporous molecular sieves plays an important role in determination of the catalyst activity.[106]

1.5. Immobilization of metal complexes

Homogeneous transition-metal catalysts are ideal for controlling reactivity and selectivity. The problem is that these catalysts are difficult to separate from the product to recycle. Because of that, heterogeneous catalysts are more desirable for use in industrial processes. But many heterogeneous catalysts show low selectivity and low activity. These drawbacks need to be overcome. One method of combining the advantages of both homogeneous and heterogeneous catalysis is to immobilize homogeneous catalysts. This can be realized by attaching homogeneous catalysts either to organic polymers[107] or to inorganic supports[108] in a manner that the ligand sphere is preserved around the metal and the complex remains accessible. Support materials for heterogenization metal (II) complexes used in this work are Mesoporous molecular sieves and Polymer-supported complexes.

1.5.1. Anchoring to inorganic supports

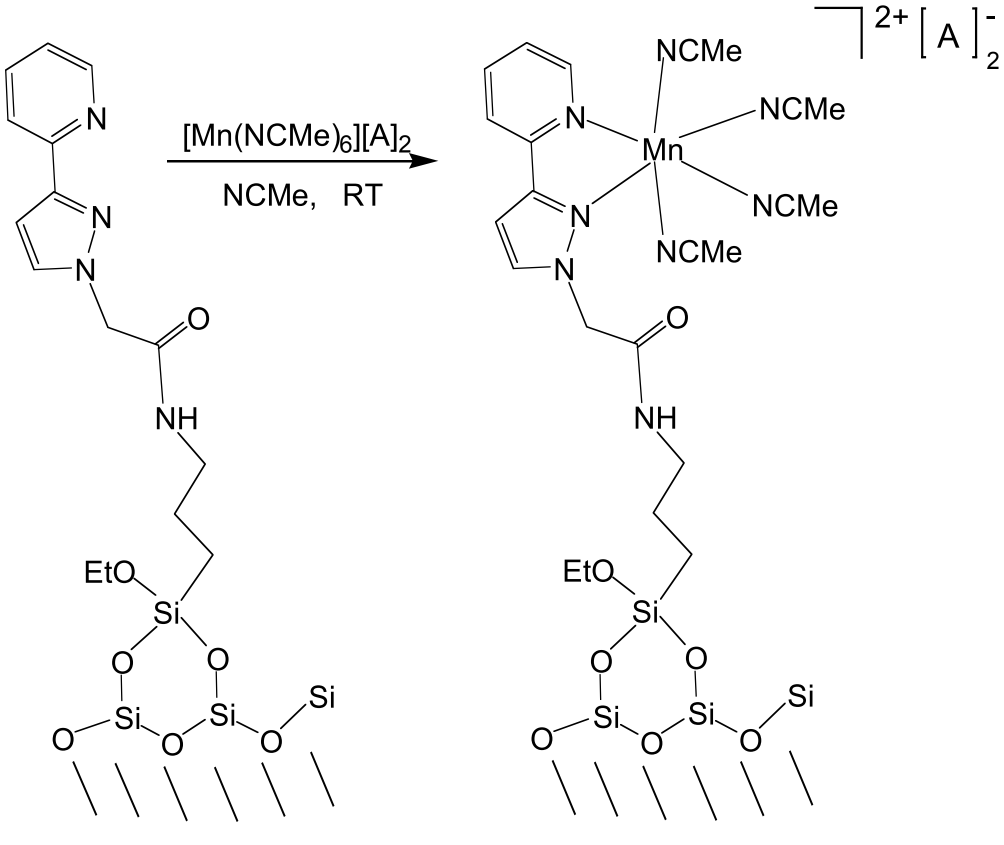
Anchoring of transition metal complexes to inorganic (silica or alumina) supports can be performed by several possibilities.[109] In the early nineties,[82, 83] scientists from the Mobil Oil Corporation synthesized ordered mesoporous materials of the M41S, family to which MCM-41 belongs. The so-called MCM (Mobile Crystalline Material) is a silicate obtained by a template mechanism.[82-85] it is ordered to certain degree. So that there are no intersecting hexagonal channels, evidenced by TEM, XRD, and vapour adsorption. By changing the length of the template molecule, the width of the channels can be controlled to be within the range of 2 - 10 nm. The walls of the channels are amorphous SiO_2. MCM-41 has attracted the attention of scientists due to its large surface area, high thermal and hydrothermal stability, possibility of controlling its pore size and its hydrophobicity and acidity. The diameters of the hexagonally packed mesopores can be precisely tuned between 2 and 15 nm by suitable modification of the pre- or postsynthetic procedure.[87] They possess a very narrow pore-size distribution, a high surface area (~1000 m^2/g), and a high pore volume (~0.8 cm^3/g) (estimated via analysis of the cryogenic nitrogen adsorption isotherm). The surface properties can be easily modified by depositing guest species on the surface or in the silicate framework.[88-91] These characteristics have also made MCM-41 a promising material as a catalyst and/or support and to be used in industrial processes of adsorption, ion exchange and environmental control.[93-100] recently developed mesoporous silicate known as SBA-15 [110] with a regular pore size, a large surface area, a large number of surface silanol groups, and a high chemical and thermal stability, is a very promising candidate as a catalyst support. [111-118]

One possibility of anchoring transition metal complexes to inorganic supports is what called Direct grafting by substitution of a metal-bonded nitrile group by surface bound hydroxl group leads to a reduction of the Lewis acidity of the metal by the formation of a –O–M bond and the loss of HA, where A is one of the counter ions of the former transition metal cation.[119]

The disadvantage of the reduction of the metal charge is usually associated with a pronounced activity loss.[120] Another possibility to heterogenize cations is the exchange of one or two nitrile ligands by a neutral, surface-fixed Lewis basic donor ligand.[63] It was quickly realized, however, that the additional electron density given by a bidendate Lewis base ligand also reduces the catalytic activity of the cation and again leads to weakly or totally inactive catalysts. A third procedure that avoids the drawbacks of the above-mentioned methods is grafting by ionic interactions. This means the partial ion exchange of H^+ or Na^+ cations present in the surface of mesoporous materials by the transition metal cations.[121]

Monometallic acetonitrile complexes $[M(MeCN)_4][BF_4]_2$ ($M = Mn^{II}$, Fe^{II}, Co^{II}, Ni^{II}, Cr^{II} and Zn^{II}) were reacted with purely siliceous MCM-41 in acetonitrile.[122] Composite materials, in which solvent-stabilized cationic metal centres are isolated and well dispersed on the silica surface, were obtained. The structural integrity of the MCM-41 material was confirmed by powder XRD and N_2 adsorption isotherms. FT-IR spectroscopy suggested that the mechanism of surface attachment possibly involves a weak interaction with single nucleophilic silanol groups at the MCM surface. All heterogenized complexes show a lower activity for cyclopentadiene polymerization than the complexes in homogeneous phase. This may be due to a certain difficulty of the substrate to reach the growth sites of the polymers. Other possible explanations can be that the polymer gets stuck in the pores of MCM-41 or covers the surface of the material.

Kühn *et. al.*[63] immobilized the manganese complex $[Mn(NCCH_3)_6][B(C_6F_5)_4]_2$ in MCM-41 derivatized with a pyrazolylpyridine ligand (scheme 1.9). This material has been characterized by elemental analysis, powder X-ray diffraction (XRD), thermogravimetric analysis (TGA), N_2 adsorption and IR/Raman spectroscopy. *Ab initio* calculations have also been carried out in order to aid interpretation of the vibrational spectra. This work has demonstrated that MCM-41 functionalized with a pyrazolylpyridine ligand is a suitable support for the immobilization of a well-defined Mn^{II} complex. The overall charge is maintained and this should ensure that the anchored complex exhibits a higher activity as an initiator for cationic polymerization than that observed when acetonitrile complexes with BF_4^- counter ions were immobilized by direct grafting with purely siliceous MCM-41. In the latter case the charge of the complex is reduced from +2 (in homogeneous phase) to +1 after heterogenization, due to the reaction with surface silanol groups. A successful heterogenization of the initiator should enable an easier separation of unreacted starting material (substrate), initiator and product than a homogeneous phase initiator.



Scheme 1.9. Synthesis of MCM-41-PP/Mn [A = $B(C_6F_5)_4^-$].

In the nineties, *McCann et al.*[54, 65, 120] anchored the dimolybdenum(II,II) salts $[Mo_2(\mu\text{-}O_2CMe)_2(MeCN)_6][BF_4]_2$ and $[Mo_2(MeCN)_8][BF_4]_4$ on SiO_2. The initial anchoring of the complexes was thought to occur at the surface silanol groups by removal of labile MeCN ligands from the complexes. These materials were poorly characterized and there was no direct physical evidence for the exact nature of the molybdenum species on the surface, that is, whether the Mo-Mo-bond is retained (as reported for $[Mo_2(\mu\text{-}O_2CMe)_4]\text{-}SiO_2$[108]) or broken to yield mononuclear species (as observed for $[Mo_2(C_3H_5)_4]\text{-}SiO_2$[123]) (see figure 1).

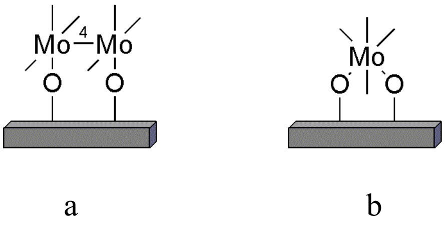
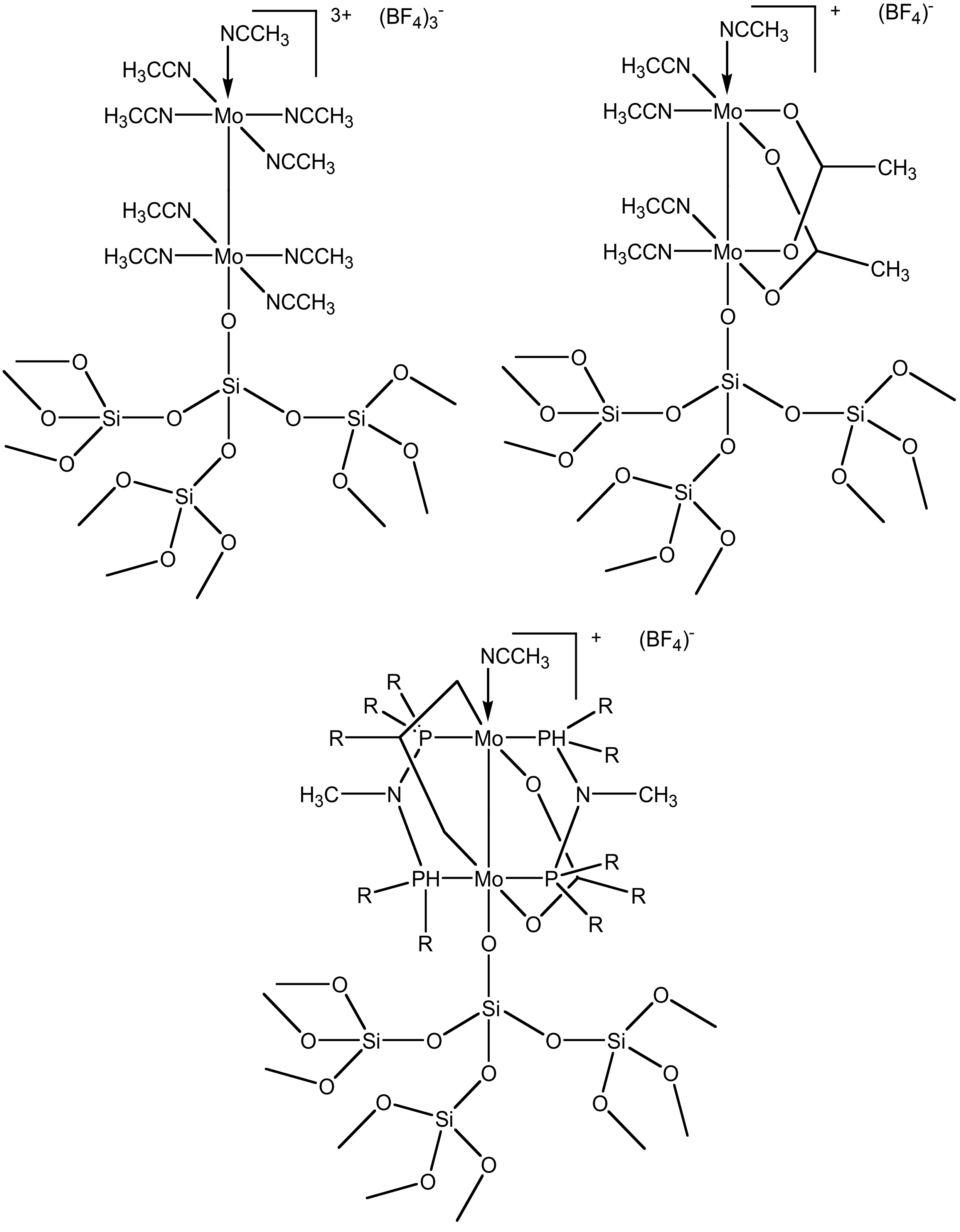


Figure 1: Anchoring of a dimolybdenum (II,II) complex onto a silica surface (a)bipodal anchoring; (b) anchoring after rupture of the Mo-Mo bond).

The supported complexes were applied to polymerize norbornene.[54, 65] In absence of the co catalyst $EtAlCl_2$, $[Mo_2(MeCN)_8][BF_4]_4\text{-}SiO_2$ was the only species able to polymerize norbornene, and at 90 ºC and a reaction time of 48 h the polymerization was essentially quantitative. When the reaction was performed at 120 ºC, a mixture of chloroform-soluble (48%) and chloroform-insoluble (50%) polymers was obtained. A soluble polymer with high *cis* content was formed using the supported catalyst. It was envisaged that the anchoring of the catalyst onto silica creates a steric congestion around the active molybdenum atoms. This crowding, in turn, causes the incoming monomer molecule to approach the catalytic centres in a way that is favourable for the formation of *cis* rather than *trans* conformations in the growing polymer.

The dimolybdenum salts supported on silica were also tested for the polymerization of cyclopentadiene.[120] The main effect of supporting the dimolybdenum salts on silica was to severely decrease their catalytic activity. McCann and Coda suggested that substantial structural and electronic changes occur during the grafting process. In spite of their poor catalytic activities, these catalysts may be reused many times to polymerize different batches of monomer.

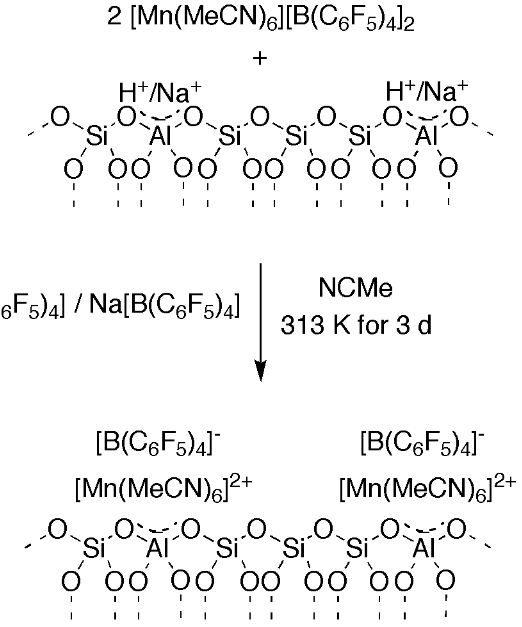
Recently, a study of the heterogenization of the dimolybdenum complexes $[Mo_2(MeCN)_{10}][BF_4]_4$, $[Mo_2(\mu\text{-}O_2CMe)_2(MeCN)_6][BF_4]_2$ and $[Mo_2(\mu\text{-}O_2CMe)_2(dppa)_2(MeCN)_2][BF_4]_2$ on the surface of purely siliceous MCM-41 was presented.[123] MCM-41 consists of a hexagonal arrangement of cylindrical pores embedded in a matrix of amorphous silica.[124, 125] The pore diameters are tunable in the range 20–100 Å and the best materials have high surface areas (>1000 m^2 g^{-1}), high pore volumes (>1 cm^3 g^{-1}) and very narrow pore size distributions. Like the commonly used silica and alumina supports, the inner surfaces of MCM-41 are covered with nucleophilic silanol groups, which enable the immobilization of transition metal catalysts by direct grafting with organometallic and transition metal complexes. The quadruply bonded dimolybdenum complex salts $[Mo_2(MeCN)_{10}][BF_4]_4$, $[Mo_2(\mu\text{-}O_2CMe)_2(MeCN)_6][BF_4]_2$ and $[Mo_2(\mu\text{-}O_2CMe)_2(dppa)_2(MeCN)_2][BF_4]_2$ react with purely siliceous MCM-41 in acetonitrile to give unstable composite materials in which solvent-stabilized cationic molybdenum fragments are isolated and well dispersed on the silica surface. Powder XRD and N_2 adsorption studies confirm that the textural properties of the high surface area mesoporous host are retained throughout the grafting process. ^{13}C CPMAS NMR and FT-IR spectroscopic studies indicate that the mechanism of surface attachment involves the displacement of labile acetonitrile ligands, most likely in the axially coordinated position, from the complexes by reaction with isolated nucleophilic silanol groups at the silica surface. It can be inferred from the spectral data and shown by X-ray absorption fine structure spectroscopy (XAFS) measurements (chart 1.3) that the molybdenum-molybdenum bond is intact in all the functionalized solids and that the complexes exhibit only a weak interaction with the surface. In the derivatized materials, the surface coverage of Mo atoms was in the range 0.15 to 0.3/nm^2, somewhat lower than the value for the concentration of free hydroxyls on the surface of pristine MCM-41. The low loading could be due to steric crowding of the guest complexes, which may prevent reaction with a large fraction of surface silanol sites. It has been estimated from the ^{29}Si CPMAS NMR that 8–27% of the silicon atoms in MCM-41 have pendant OH groups and that the average separation of these groups is in the range 5 to 10 Å. It seemed unlikely, therefore that the dimolybdenum complexes could undergo bipodal anchoring to the silica surface, as suggested by McCann *et al.* [54] for silica fixed $[Mo_2(MeCN)_{10}][BF_4]_4$ and $[Mo_2(\mu\text{-}O_2CMe)_2(MeCN)_6][BF_4]_2$ complexes (Chart 1.3). A monopodal anchoring was suggested as the dominant mechanism for surface attachment (Chart 1.3). In order to study the local structure around molybdenum in the supported materials, Mo K-edge X-ray absorption fine structure spectroscopy (XAFS) was carried out.[43] It was shown that the Mo-Mo quadruple bond is retained in the grafted species and that no significant change occurs in the ligands surrounding the $[Mo\text{-}Mo]^{4+}$ core. Furthermore, the catalytic activity of the MCM-41-supported $[Mo_2(\mu\text{-}O_2CMe)_2(MeCN)_6][BF_4]_2$ was tested. The initiator activity is only slightly reduced by the heterogenization in the case of the $[Mo\text{-}Mo]^{4+}$ type complexes which were examined.



$R = C_6H_5$

Chart 1.3. Monopodal anchoring of a dimolybdenum (II,II) complex onto silica surface.

Kuehn et al. grafted some of Cu & Mn complexes by the 3rd method of anchoring transition metals complexes on inorganic supports like H-AlMCM-41, Na-AlMCM-41, H-AlMCM-48 or Na-AlMCM-48 by the partial ion exchange of H^+/Na^+ cations present in the mesoporous materials surface (see scheme 10).



Scheme 10: Anchoring of $[Mn(MeCN)_4][B(C_6F_5)_4]_2$ on a mesoporous silica surface.[121]

Such a heterogenization method should not lead to a pronounced activity loss, since the cation and one of the non-coordinating anions remain largely unchanged. Until now, three different systems are known in literature: $[Mn(MeCN)_6][B(C_6F_5)_4]_2$ grafted on H-AlMCM-41/48 or Na-AlMCM-41/48[121] and $[Cu(MeCN)_6][B(C_6F_5)_4]_2$[126] as well as $[Cu(MeCN)_4][BF_4]_2$[127] heterogenized on Na-AlMCM-41 or Na-AlMCM-48.

Polymerization test reactions for $[Mn(MeCN)_6][B(C_6F_5)_4]_2$ complex has been carried out for the polymerization of isobutene. The samples prepared on Na-AlMCM41/48 show higher catalytic activity (6–8% product yield) than the samples prepared on H-AlMCM-41/48 (3–5% product yield).

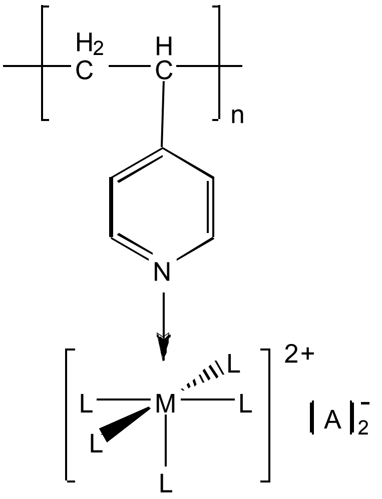
The grafted $[Cu(MeCN)_4][BF_4]_2$ was tested for the cyclopropanation of olefins. In all cases, the catalytic activities in homogeneous medium are higher than the activities observed in heterogeneous phase and Na-AlMCM-48 grafted materials achieve better performances than the ones grafted on the one-dimensional Na-AlMCM-41 structure. Recyclability tests show a considerable decrease of activity during the second run while the activity remains largely stable for further catalytic runs. This could be due to initial partial leaching of the weakly bonded complex. A further factor might be the absorption of reactant/product molecules on the active species of the surface.

1.5.2. Anchoring to Polymer supports

The development of polymer-supported and insoluble (heterogeneous) transition metal catalysts has attracted a great deal of attention in organic chemistry due to the major advantage of the physical separation of the supported reagent from the substrates and products, thereby allowing the recycling of expensive catalysts (e.g., noble metals) or of toxic products and is of prime economic and environmental importance. Polymer-supported catalysts are of easily accessible complexing functionalities allowing the stability and uniformity of the obtained materials.[128-130]

Several types of polymers that have N-heterolytic carbene moieties, such as poly(4-vinylpyridine) (P4VP), have been examined to create stable carrier-catalyst interactions. Much work has been done aimed to heterogenize metal transition complexes on P4VP in the last decade. For example, sodium ruthenate was supported on 2 % and 25 % cross-linked poly(4-vinylpyridine). These compounds were found to be efficient and selective for the room temperature oxidation of internal and external alcohols to aldehydes and ketones, respectively.

The catalysts were active with a wide range of co-oxidants and no over-oxidized products were observed.[107]



Char 1.4. A donor-acceptor interaction in P4VP-supported metal (II) complexes in the octahedral system

It has been demonstrated that P4VP has the ability to form complex with metal ions. P4VP is also a strong coordinating ligand that can compete for binding the metal catalyst systems where there is a possibility of the formation of pyridine-coordinated metal ion complexes in the polymerization solution.[131] The synthesis of polymer-supported metal(II) complexes based on the donor-acceptor interaction between the pyridine nitrogen atoms and the metal centre.[132-134] The nitrogen atoms on the pyridine ring of P4VP act as proton acceptor (Chart 1.4).[135]

1.6. Objectives of this work

It has been found that transition metals complexes of the formula $[M(NCCH_3)_4][BF_4]_2$ (M^{II} = Cr, Mn, Fe, Co, Ni, Cu, Zn) and some of their second and third row congeners show good activities as initiators in the cationic polymerization of cyclopentadiene and methylcyclopentadiene both in homogeneous and heterogeneous phase. But not active in the polymerization of other monomers, e.g. isobutene, even at elevated temperatures.

Changing the counter anion $(BF_4)^-$ by more weakly coordinating anions like $[B(C_6H_3(m\text{-}CF_3)_2)_4]_2$ and $[B(C_6F_5)_4]_2$ (chart 1.5) leads to an extremely high active catalyst for cyclopentadiene polymerization, and also enables the polymerization and copolymerization of other monomers, among them isobutene. The best initiator activities observed previous to this work are displayed by manganese(II) complexes of the general formulae $[Mn(NCCH_3)_6][N_2C_3H_3(B(C_6F_5)_3)_2]_2$, $[Mn(NCCH_3)_6][B(C_6H_3(m\text{-}CF_3)_2)_4]_2$ and $[Mn(NCCH_3)_6][B(C_6F_5)_4]_2$.

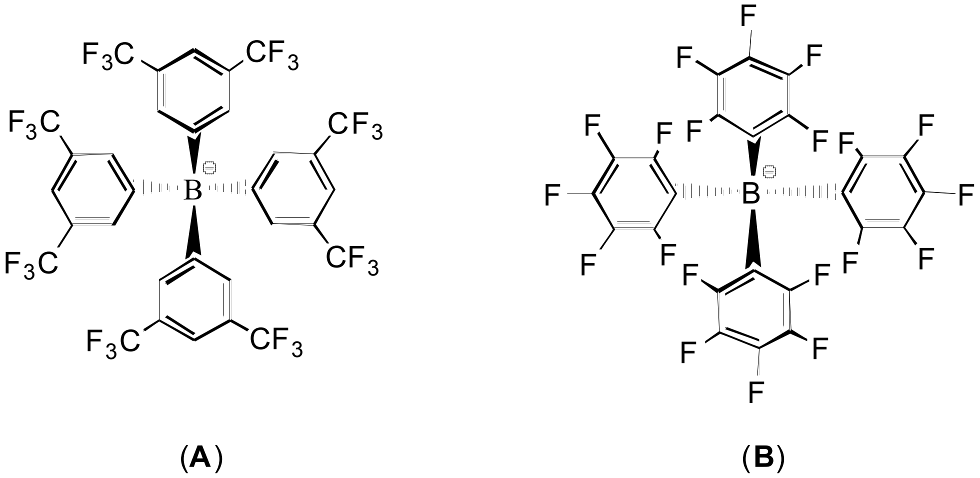


Chart 1.5. Structures of the non-coordinated counter anions (A) $[B\{C_6H_3(CF_3)_2\}_4]^-$ and (B) $[B(C_6F_5)_4]^-$

Therefore, the objective of this work was to replace the Mn metal with other first row transition metals in order to achieve more active initiator complexes for polymerization reactions.

The acetonitrile ligated copper complexes of the type $[Cu(NCCH_3)_n][A]_2$ (A = $B(C_6F_5)_4$, and $B\{C_6H_3(m\text{-}CF_3)_2\}_4$) are found to be active in catalyzing isobutene polymerization in homogeneous phase. Immobilization of homogeneous copper complexes has then become the main issue in this respect, in order to combine advantages of homogeneous catalysis and heterogeneous catalysis. Immobilization of copper (II) acetonitrile complexes onto inorganic supports (MCM-41 and SBA-15) and organic supports (polymer), and their catalytic activity and recyclability for olefin cyclopropanation and aldehydes olefination reactions were examined.

Further research, closely related to the work presented in this thesis has been carried out in co-operation with our industrial partner BASF AG. However due to the sensitive nature of the findings and secrecy agreements signed, the work cannot be reported yet. These findings are now under evaluation and will be published at a further date.

2. Synthesis and Characterization of Acetonitrile Ligated Transition Metal Complexes with Tetrakis{(pentafluoro -phenyl)}borate as Counteranions

2.1. Background

First row transition metal complexes of general formula $[M(NCCH_3)_6][A]_2$ (M^{II} = Cr, Mn, Fe, Co, Ni, Cu, Zn; A = counter anion) and some of their dimeric second and third row congeners of formula $[M_2(NCCH_3)_{8-10}][A]_2$ (M^{II} = Mo, Tc, Re, Rh; A = counter anion) are known for many years.[1, 2] Several groups have contributed to their synthesis. These complexes are synthetically important as starting materials and some compounds of that type have been successfully applied as initiators or catalysts in polymerization reactions. Generally, they can be synthesized by two methods: (1) by salt metathesis of silver precursors; Potassium salts and amine salts are used to introduce the Weakly Coordinating anions (WCAs) into the organonitrile complexes.[3] and (2) through the reaction of metal halides with BCl_3, $AlCl_3$, $GaCl_3$. $InCl_3$, $TlCl_3$ and $FeCl_3$, respectively, to form complexes of the general formula $M(NCCH_3)_x^+(M'Cl_4)_y^-$.[4] In order to obtain acetonitrile ligated compounds, all reactions are to be carried out in nitrile solutions.

It has been 30 years since the term “non-coordinating anion”[5] was coined to describe anions such as ClO_4^-, NO_3^-, and BF_4^-, which are usually found to be non-coordinating (or weakly coordinating) in aqueous solution. In the last three decades, a plethora of species that closely resemble non-coordinating anions has been synthesized. Most of them are actually weakly coordinating (so called “weakly coordinating anions”, WCAs) in many cases. In order to develop anions with even weaker coordination abilities, the negative charge has to be delocalized over a large area of non-nucleophilic and chemically robust moieties. WCAs have found manifold and meanwhile well established applications, e. g. in the group 14 metallocene-based and related olefin-polymerization.[6]

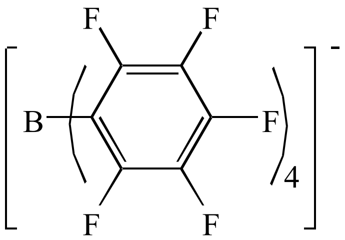
There are several common strategies to introduce WCAs into a salt. Silver salts of WCAs may oxidize transition metal complexes with a medium oxidation potential and transition-metal salts of WCAs are found at the same time.[7] The abstraction of a methyl-group from $[Cp_2M(CH_3)_x]$ (M = Ti, Zr, Hf, Ta; x = 2, 3) by strong organometalic Lewis acids like $B(C_6F_5)_3$ produces the tight ion pair $[Cp_2MMe]^+[MeB(C_6F_5)_3]^-$.[8] WCAs can also be introduced into a system through metathesis reactions of $M^+[X]^-$ ($[X]^-$ = WCA, M = univalent metal, such as Li, Na, K, Ag, Tl) with labile or sometimes even covalently bound halides. In many cases, Ag^+ is the best cation to abstract the halide from the substrate. Silver salt metathesis is a well established method of halide ion abstraction. Its origin dates back to the earliest days of coordination chemistry. Since a long time, silver nitrate has been used as a standard testing reagent to differentiate between free and complexed chloride. Until today the availability of numerous silver salts of WCAs, AgY (Y = ClO_4^-, SbF_6^- etc), has kept silver salt metathesis a widely applied method of halide ion abstraction from labile sources. For the synthesis of versatile types of luminescent heterometallic materials in supramolecular chemistry, compounds of the type $[M(NCCH_3)_4][A]$ (M = Ag; A = BF_4^-, PF_6^-, ClO_4^-, etc) have been utilized as starting materials.[9] Complexes of general formula $[M(NCCH_3)_{2\text{-}6}][A]_{1\text{-}2}$ can be used as catalysts in the cationic polymerization of cyclopentadiene and methylcyclopentadiene in both homogeneous and heterogeneous phase.[10] The successful synthesis of a series of acetonitrile complexes of the type $[M(NCCH_3)_6][A]_2$ where A = $B(C_6F_5)_4^-$, $B\{C_6H_3(m\text{-}CF_3)_2\}_4^-$, $((C_6F_5)_3B\text{-}C_3H_3N_2\text{-}B(C_6F_5)_3)^-$, exhibiting excellent activities for the polymerization of isobutene has been reported.[11]

In this work the synthesis and characterization of complexes of general formula $[M(NCCH_3)_6][A]_2$ (M^{II} = Cr^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, [A] = $[B(C_6F_5)_4]^-$ in the solid state and solution is reported, together with a brief report on the catalytic behaviour of these compounds.

2.2. Results and discussion

2.2.1. Synthesis and textural Characterization

$[B(C_6F_5)_4]^-$ (Scheme 1) was prepared by reacting pentafluorophenyl bromide with *n*-butyllithium in the presence of KCl (Equation 1a-1c) forming the corresponding potassium salt. The potassium salt was then transformed to the silver salt by reaction with silver nitrate (Equation 1d).



Scheme 1

$$\text{R-Br} + \text{nBuLi} \xrightarrow[-78\ ^{o}\text{C}]{\text{Et}_2\text{O}} \text{RLi} + \text{nBuBr} \tag{1a}$$

$$4\ \text{RLi} + \text{BCl}_3 \xrightarrow[-78\ ^{o}\text{C}]{} \text{Li}[\text{B(R)}_4] + 3\ \text{LiCl} \tag{1b}$$

$$\text{Li}[\text{B(R)}_4] + \text{KCl} \xrightarrow[\text{r.t.}]{} \text{K}[\text{B(R)}_4] + \text{LiCl} \tag{1c}$$

$$\text{K}[\text{B(R)}_4] + \text{AgNO}_3 \xrightarrow[\text{r.t.}]{\text{CH}_3\text{CN}} \text{Ag}[\text{B(R)}_4] + \text{KNO}_3 \tag{1d}$$

R= Pentafluorobenzene bromide

Compounds **(1-6)** were synthesized by reacting metal(II) halides with the silver salts of the corresponding anion in acetonitrile (anion exchange) (Equation 2). The solvent stabilized complexes are moderately air stable and can therefore be handled in laboratory atmosphere for brief periods of time (minutes). For storage over longer periods of time (months), the compounds have to be kept under an inert gas atmosphere at low temperatures (- 35 °C).

$$MX_2 + 2\,Ag[B(C_6F_5)_4] \xrightarrow[\text{r.t.}]{CH_3CN} [M(NCCH_3)_6][B(C_6F_5)_4]_2 + 2\,AgX$$

M = Cr **(1)**, Fe **(2)**, Co **(3)**, Ni **(4)**, Cu **(5)**, Zn **(6)**
X = Cl, Br

All synthesized compounds were characterized by IR spectroscopy, ^{1}H-NMR spectroscopy, thermogravimmetry and elemental analysis (EA).

Infrared Spectroscopic (IR) Analysis

The infrared (IR) spectra of the complexes, recorded in a KBr matrix exhibit two sharp ν(CN) absorptions of medium intensity (assigned to the fundamental ν_2-CN stretching mode and a combination mode ($\nu_3 + \nu_4$))[1y] at approximately 2325 and 2295 cm^{-1}, respectively, as shown in Table 1.

There are, however, tow exceptions. The Zn^{II} and Cu^{II} complexes exhibit a third but weaker absorption at 2267 and 2279 cm^{-1} respectively. Such a three-peak absorption pattern had already been observed for the related complex $[Cr^{II}(NCCH_3)_6][TFPB]_2$[1y] (TFPB = tetrakis(3,5-bis(trifluoromethyl)phenyl)-borate). But is absent in the spectra of the Cr^{II} compound described here. This three peaks absorption pattern assigned to the presence of two slightly more weakly coordinating “axial” acetonitrile ligands (relative to the four other, “equatorial” acetonitriles). Also this seems unlikely for Zn^{II} complex. This assumption might also explain the lower energy of the Cr^{II} complex vibration in comparison to that of the other complexes although no third vibration was observed.

The higher energy of both types of vibrations observed for all examined compounds in comparison to free acetonitrile (ν(CN) = 2253 and 2293 cm^{-1}) is caused by σ-donation of electron density from the lone pair of the nitrogen, which has some *anti* bonding character.[1y, 12]

Keeping these compounds at room temperature for prolonged time leads the losing of one or two of the acetonitrile ligands, according to elemental analysis. However, the complexes can be obtained in their original (hexacoordinate) composition, when recrystallized from acetonitrile. The metal complexes with more strongly coordinated anions, such as $[BF_4]^-$, do not show this kind of behaviour.[1c, 3a]

Table 1. Comparison of the Infrared absorption bands of $[M(NCCH_3)_6][TPFB]_2$ and those of some previously described $[M(NCCH_3)_n][A]_2$ (n = 4, 6) complexes.

Metel	Anion, A	ν(CN) cm^{-1}			Ref
Cr	[TPFB]	2305	2278		[a]
	[TFPB]	2324	2297	2277	1y
	$[BF_4]$	2333	2305		3a
Fe	[TPFB]	2314	2284		[a]
	[TFPB]	2318	2291		1y
	$[BF_4]$	2310	2287		1c
Co	[TPFB]	2322	2296		[a]
	[TFPB]	2321	2295		1y
	$[BF_4]$	2316	2292		1c
Ni	[TPFB]	2326	2300		[a]
	[TFPB]	2326	2299		1y
	$[BF_4]$	2316	2292		1c
Cu	[TPFB]	2340	2317	2279	[a]
	[TFPB]	2332	2303	2271	11d
	$[BF_4]$	2322	2300		1c
Zn	[TPFB]	2324	2297	2267	[a]
	$[BF_4]$	2320	2295		1c

[a] This work
TPFB = Tetrakis{(penta-fluorophenyl)}borate.
TFPB = Tetrakis(3,5-bis(tri-fluoromethyl)phenyl)-borate.

Thermogravimmetry

Thermogravimmetric analysis (TGA) was executed for all compounds. The Cu complex shows its first decomposition onset at ca. 107 °C, being associated with a mass loss of 18.4 wt.%. Since an analogous decomposition step can not be found in acetonitrile free $K[B(C_6F_5)_4]$, this mass loss is likely to correspond with the loss of all of the acetonitrile ligands. These ligands contribute

14.7 wt.% of the total mass of the compound. A similar behaviour is also observed for Fe complex, associated with a loss of 13.1 wt.% at 107.8 ºC. Cr and Zn complexes show a 4.1 wt.% and 4.0 wt.% mass loss at 109.6 ºC and 105.7 ºC respectively. These decomposition steps correspond to the loss of two acetonitrile ligands (4.9 wt.%) in each case. Both complexes also show a second acetonitrile loss at 160.7 ºC (5.7 wt.% (two $NCCH_3$ ligands [4.9 wt.%])) and 178.3 ºC (10.4 wt.% (four $NCCH_3$ ligands [9.8 wt.%])) respectively. Co and Ni complexes show their first decomposition steps above 200 ^{0}C and account for ca. 78.2 wt.% and 71.3 wt.% mass loss, respectively. Accordingly, these steps must account for both the losses of all acetonitrile ligands and additionally for anion fragmentation. The Ni complex has the highest thermal stability while the Zn complex has the lowest thermal stability of all examined compounds. The decomposition behaviour of the Mn complex was reported earlier.[11] It shows first decomposition step at 178.5 ºC with a 14.0 % wt. loss corresponding to the loss of all six $NCCH_3$ ligands (14.1 wt.%). The second step was observed at 260.3 ºC with a loss of 64.1 wt.%. The TGA results are summarized in Figures 1 and 2 and table 2. As can be deduced from these data, the thermal stability sequence is Ni > Co > Mn > Cr > Fe > Cu > Zn.

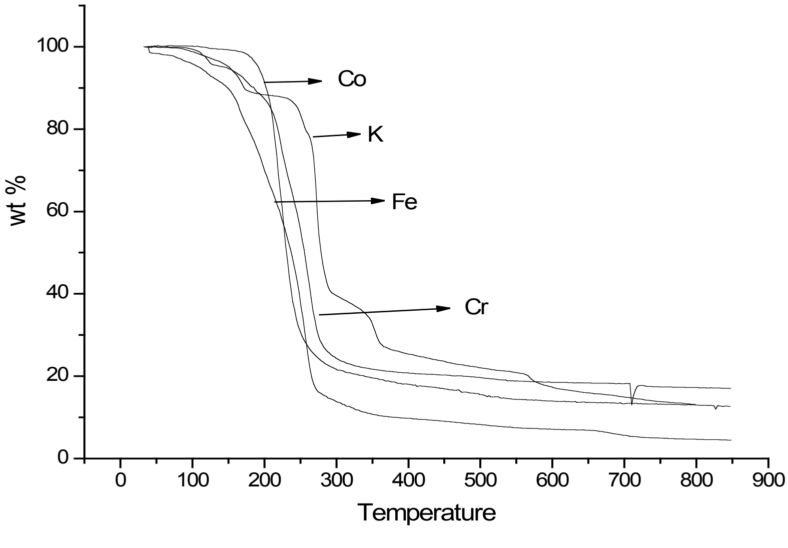


Figure 1. TGA of the K[TPFB] and $[M^{II}(NCCH_3)_6][TPFB]_2$ complexes. [M = Co, Fe, Cr]

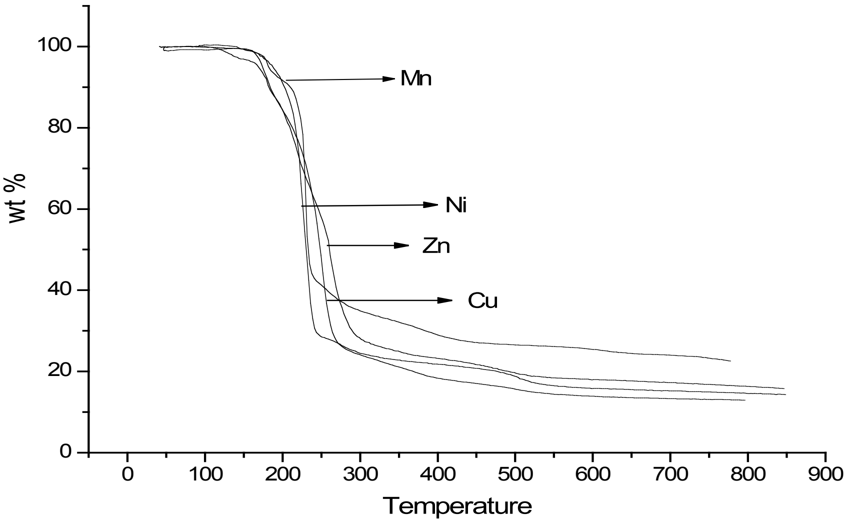


Figure 2. TGA of the $[M^{II}(NCCH_3)_6][TPFB]_2$ complexes. [M = Mn, Ni, Zn, Cu]

Table 2. Thermogravimetric analyses of the $[M(NCCH_3)_6][TPFB]_2$ complexes between room temperature and 850 °C with a heating rate of 10 ^{0}C/min.

Metal	$T_{onset}{}^{o}C$	Wt. loss%	$T_{onset}{}^{o}C$	Wt. loss%	$T_{onset}{}^{o}C$	Wt. loss%	$T_{onset}{}^{o}C$	Wt. loss%	$T_{onset}{}^{o}C$	Wt. loss%	Total loss%
Cr	109.6	4.1	160.7	5.7	213.4	25.4	250.9	40.8	298.4	5.2	84.0
Mn	178.5	14.0	260.3	64.1	-	-	-	-	-	-	85.0
Fe	107.8	13.1	191.0	22.7	247.1	47.9	-	-	-	-	95.0
Co	207.3	78.2	305.7	5.4	-	-	-	-	-	-	85.8
Ni	211.2	71.3	238.2	7.7	288.3	7.0	-	-	-	-	85.5
Cu	106.6	18.4	161.4	17.5	179.1	7.4	257.2	9.1	344.8	14.8	83.5
Zn	105.7	4.0	178.3	10.4	259.8	39.2	259.7	26.8	-	-	84.3

The Fe complex looses the highest relative mass within the examined temperature interval. The total weight loss observed is ca. 95 wt.%, correlating with the expected mass for a residual of composition FeF_2 (5.7 %; EA evidence). Thus, the metal seems to react with anion fragments after the complete loss of the solvent. The other complexes display incomplete decomposition. For sake of comparison with another non coordinating counter anion, table 3 shows the TGA of

$[M^{II}(NCCH_3)_6][TFPB]_2$[1y] (M = Ni, Co, Fe, Mn, Cr, V, [TFPB] = tetrakis[3,5-bis(trifluoromethyl)phenyl]-borate).

Table 3. Thermogravimetric analyses of $[M(NCCH_3)_6][B\{(C_6H_3)(m\text{-}CF_3)_2\}_4]_2$[1y] salts between room temperature and 450 °C with a heating rate of 15 °C/ min.

Metal	Weight loss <100 °C		Weight loss >100 °C			Total % loss
	T_{onset} [°C]	% loss	T_{onset} [°C]	T_{onset} [°C]	T_{onset} [°C]	
Cr	ambient	2.2	131	159	211	85.1
Mn	[a]		139	167	220	84.2
Fe	ambient	1.5	143	180	221	84.4
Co	ambient	1.4	145	[a]	168	85.5
Ni	ambient	1.6	146	160	185	95.1

[a] Not resolved.

As it can be seen by comparing tables 2 and 3, there are some differences in the thermal stability of the complexes, seemingly dependent on the type of the non coordinating counter anion. For the Ni complex, total decomposition is observed (95.1 % wt. loss) when [TFPB] is the counter anion, while in the case of [TPFB] a residue of higher mass is obtained (85.5 % wt. loss). This behavior is different from that of Fe complex with 95 % wt. loss when [TPFB] is the counter anion. It is interesting to note that all the metal complexes coordinated with [TFPB] decompose below 100 °C with a loss of ca. 1 $NCCH_3$ ligand. In the case of [TPFB], all the complexes begin to decompose above 100 °C with different fragmentations. It may be concluded that the complexes with [TPFB] as the counter anion are somewhat more stable than those having [TFPB] as counter anion.

The electronic absorptions are measured for all complexes prepared in this work. The values are comparable with those of the $[M^{II}(OH_2)_6]^{2+}$ ions,[13] but are shifted to higher energies. This is in agreement with acetonitrile being a stronger field ligand than water in the spectrochemical series. The molar extinction coefficients (ε) range from 1.0 to 49.1 $cm^{-1}M^{-1}$. The molar extinction coefficients values for $[M^{II}(NCCH_3)_6]^{2+}$ ions are greater than those of the $[M^{II}(OH_2)_6]^{2+}$ ions. This is due to the increase in vibronic coupling of coordinated $NCCH_3$ compared to water.[12a] Table 4 shows the values for all the $[M^{II}(NCCH_3)_6]^{2+}[TPFB]_2^-$ complexes.

The Ni complex has three absorptions consistent with an octahedral coordination[1c] [e.g. $Ni(NH_3)_6^{2+}$ absorbs at 28200, 17500 and 13150 cm^{-1}; $[Ni(NCCH_3)_6]^{2+}$ $[BF_4]^-_2$ absorbs at 27560, 17090 and 13940 cm^{-1}; $[Ni(NCCH_3)_6]^{2+}$ $[TFPB]^-_2$ absorbs at 27500, 17200 and 10400 cm^{-1}]. The Cu complex has a single absorption, which is consistent with a distorted octahedral coordination [3a] [e.g. $[Cu(NCCH_3)_6]^{2+}$ $[BF_4]^-_2$ absorbs at 13320 cm^{-1}]. The Fe complex has one single absorption in comparison with $[Fe(NCCH_3)_6]^{2+}$ $[BF_4]^-_2$, which absorbs at 10965 cm^{-1} [3a] and with $[Fe(NCCH_3)_6]^{2+}$ $[TFPB]^-_2$, which absorbs at 10900 cm^{-1}. [1y] The Cr complex shows one absorption at 16638 cm^{-1} in comparison to $[Cr(NCCH_3)_6]^{2+}$ $[TFPB]^-_2$ at 15500 cm^{-1}. [1y]

Table 4. UV-Visible data for $[M^{II}(NCCH_3)_6][TPFB]_2$ in MeCN

Complex	wave length (nm)	wave number (cm^{-1})	abs.	ε[*] (cm^{-1}M^{-1})
$[Cr(NCCH_3)_6]^{2+}$	601	16639	0.09123	30.4
$[Fe(NCCH_3)_6]^{2+}$	892	11211	0.10650	35.5
$[Co(NCCH_3)_6]^{2+}$	679	14728	0.05225	26.1
	613	16313	0.04759	23.8
$[Ni(NCCH_3)_6]^{2+}$	679	14728	0.01388	6.9
	627	15949	0.01533	7.7
	363	27548	0.02301	11.5
$[Cu(NCCH_3)_6]^{2+}$	774	12920	0.09834	49.2
$[Zn(NCCH_3)_6]^{2+}$	853	11723	0.00969	3.2
	386	25907	0.00305	1.0

[*] Concentrations were between 1.5-3.0 mM in acetonitrile, path length of 1 cm, background was solvent vs. solvent.

The ^1H-NMR (400 MHz, CD_2Cl_2, 25 °C) shifts corresponding to the methyl group in methylene chloride were observed as singlets at: δ = 2.14, 2.13, 2.16, and 2.42 ppm for Ni, Zn, Cr and Fe complexes respectively, slightly shifted to low field in comparison to CH_3CN (δ = 1.93 ppm). [14,15]

2.2.2. Catalytic Activity:

It is well established that 2-methylpropene (“isobutene”) can be polymerized by means of cationic initiators such as protons or Lewis acids. Typical catalysts are $AlCl_3$, BCl_3, BF_3 and water as co-initiator. Typical solvents are methylchloride, dichloromethane and ethene at temperatures of -80 °C or below (-100 °C in case of ethene as solvent). Polymerization under these conditions, however, is very fast and exothermic.

Complexes of formula $[M^{II}(NCCH_3)_6][TPFB]_2$ (M = Cr, Fe, Co, Ni, Zn,) have been applied as catalysts for the polymerization of 2-methylpropene under similar conditions as Mn, Mo and Cu based catalysts.[11,16] The great advantage of these catalysis is that the reaction takes place at room temperature, the product from this reaction have molecular weight from M_n = 0.5-5 Kg mol^{-1} and are colourless and honey like viscous liquid which known as low molecular weight polyisobutene.

. The polymerization reaction was carried out under these conditions, the temperature was 30 ºC, dichloromethane have been used as solvent, the catalyst concentration was $0.5x10^{-4}$ mol/l and the 2-methylpropene concentration was 1.78 mol/l.

The iron complex turns out to be the most active catalyst, reaching conversions of 88 % within 5 hours. The average molecular weight (M_n) of the product polymer is 900 g/mol, the polydispersity index (PDI) is 2.33 with 62 % of terminal double bonds (Exo End groups). The Zn complex shows almost the same reactivity but the polymerization proceeds more slowly. From the examinations of the catalyst complexes described above, it seems likely that the activity depends on the ease of loosing acetonitrile ligands from the metal centre to create free coordination sites for substrate coordination. A comparison between the activities of the catalysts is given in Table 5.

Table 5. The polymerization results for $[M^{II}(NCCH_3)_6][TPFB]_2$ complexes.[a]

Metal	Time (Hrs)	Conversion (%)	M_n	PDI	Exo End groups (%)
			g/mol		
Cr	1	2	-	-	-
Fe	0.5	20	1600	2,25	79
	1	37	1400	2,21	80
	2	64	1200	2,25	74
	4	86	1000	2,40	66
	5	88	900	2,33	62
Co	10	20	1600	1,69	-
Ni	0,5	1	-	-	-
	1	5	-	-	-
	2	15	2400	2,00	-
	5	17	1400	1,70	-
	10	35	1100	1,80	-
Zn	0,5	24	5300	1,90	71
	1	57	800	1,70	74
	2	56	1000	1,90	76
	5	88	900	1,90	58
	10	88	800	1,90	50

[a] $C_{Isobutylene}$ = 1.78 mol/l, Solvent – DCM$_{ccat}$ = $0.5x10^{-4}$ mol/l,
Temperature = 30°C.

Single crystal X-ray results

Exemplary for the examined compounds in the series of $[M(NCCH_3)_6][TPFB]_2$ the crystal structure for the cobalt complex **3** has been determined. Crystal data and details of the structure determination are presented in Figure 3 and Table 6. A search in the CSD database [17] (version 5.29, November 2007) revealed 22 hits for dicationic complexes of the type $[M^{II}(NCCH_3)_6]^{2+}$ (M^{II} = V^{2+} to Zn^{2+}). All metal centres show more or less ideal octahedral coordination. The observed deviations from the ideal case may be attributed to packing effects in the solid state. Surprisingly no data for the Jan-Teller ions Cr^{2+} and Cu^{2+} are deposited.

The results for the new investigated Co complex fits the reported values perfect. [17c]

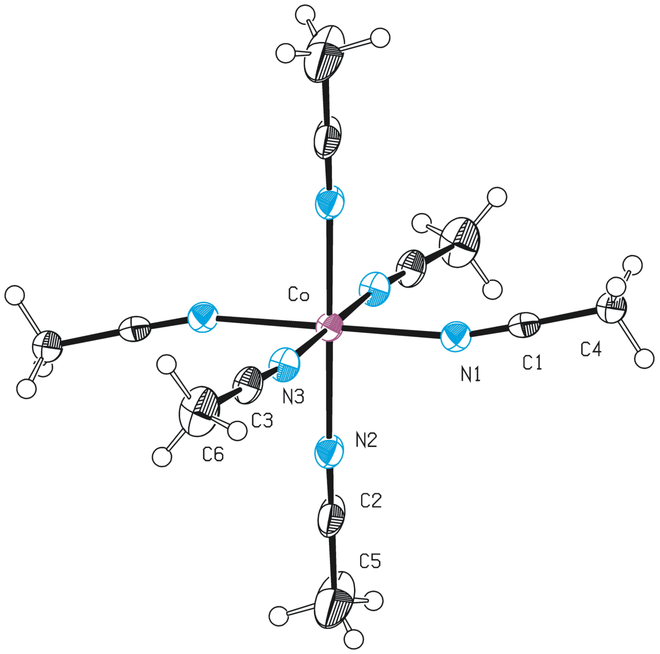


Figure 3. ORTEP style plot[18f] of the dicationic part of compound **3** The cobalt atom is located on a center of inversion. Thermal ellipsoids are drawn at the 50 % probability level. Selected bond lengths [Å] and bond angles [°]: Co–N1 2.137(1), Co–N2 2.105(2), Co–N3 2.098(2), N1–C1 1.138(2), N2–C2 1.126(3), N3–C3 1.134(2), C1–C4 1.457(3), C2–C5 1.458(6), C3–C6 1.454(3); N1–Co–N2 91.76(6) N1–Co–N3 91.63(5) N2–Co–N3 90.28(6), Co–N1–C1 165.5(2), Co–N2–C2 175.1(2), Co–N3–C3 169.0(1), N1–C1–C4 178.1(2), N2–C2–C5 179.9(2), N3–C3–C6 178.8(2).

Table 6. Crystallographic Data for $[Co(NCCH_3)_6][B(C_6F_5)_4]_2$ (**3**)

	3
formula	$C_{60}H_{18}B_2CoF_{40}N_6$
formula weight (g / mol)	1663.35
color / habit	purple / fragment
crystal dimensions (mm^3)	0.20 × 0.36 × 0.51
crystal system	triclinic
space group	$P\bar{1}$ (No. 2)
a, Å	10.8612(1)
b, Å	12.3138(1)
c, Å	12.6007(1)
α (°)	69.3894(5)
β (°)	87.7262(5)
γ (°)	85.9142(5)
V, Å^3	1573.18(2)
Z	1
T, K	123
D_{calcd}, g cm^{-3}	1.756
μ, mm^{-1}	0.439
F(000)	817
θ-range, deg	1.73 – 25.42
Index ranges (h, k, l)	±13, ±14, ±15
no. of rflns collected	34151
no. of indep rflns / R_{int}	5780 / 0.033
no. of obsd rflns ($I>2\sigma(I)$)	5190
no. of data/restraints/params	5780 / 0 / 496
$R1$ / $wR2$ ($I>2\sigma(I)$)[a]	0.0288 / 0.0693
$R1$ / $wR2$ (all data)[a]	0.0338 / 0.0719
GOF (on F^2)[a]	1.035
Largest diff peak and hole (e Å^{-3})	+0.37 / -0.32

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

$GOF = \{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$

2.3. Conclusion

Complexes of formula $[M^{II}(NCCH_3)_6][TPFB]_2$ (M = Cr, Fe, Co, Ni, Cu and Zn) have been prepared and characterized. All compounds are easily accessible and can be obtained in good yields. From the FT-IR absorptions can be concluded that the some of the complexes have a distorted structures. Upon thermolysis, solvent is lost from the coordination sphere together with abstraction of fluoride from the anion. However, different bond strengths of acetonitrile ligands attached to the same metal centre is not clearly obvious from the TG-MS results. All complexes were applied as catalysts for the polymerization of 2-methylpropene at room temperature. Products with molecular weights between 800 and 5300 g/mol and with high contents of terminal double bonds between 50 and 80 % are available by this reaction, with the iron compound being the most active catalyst.

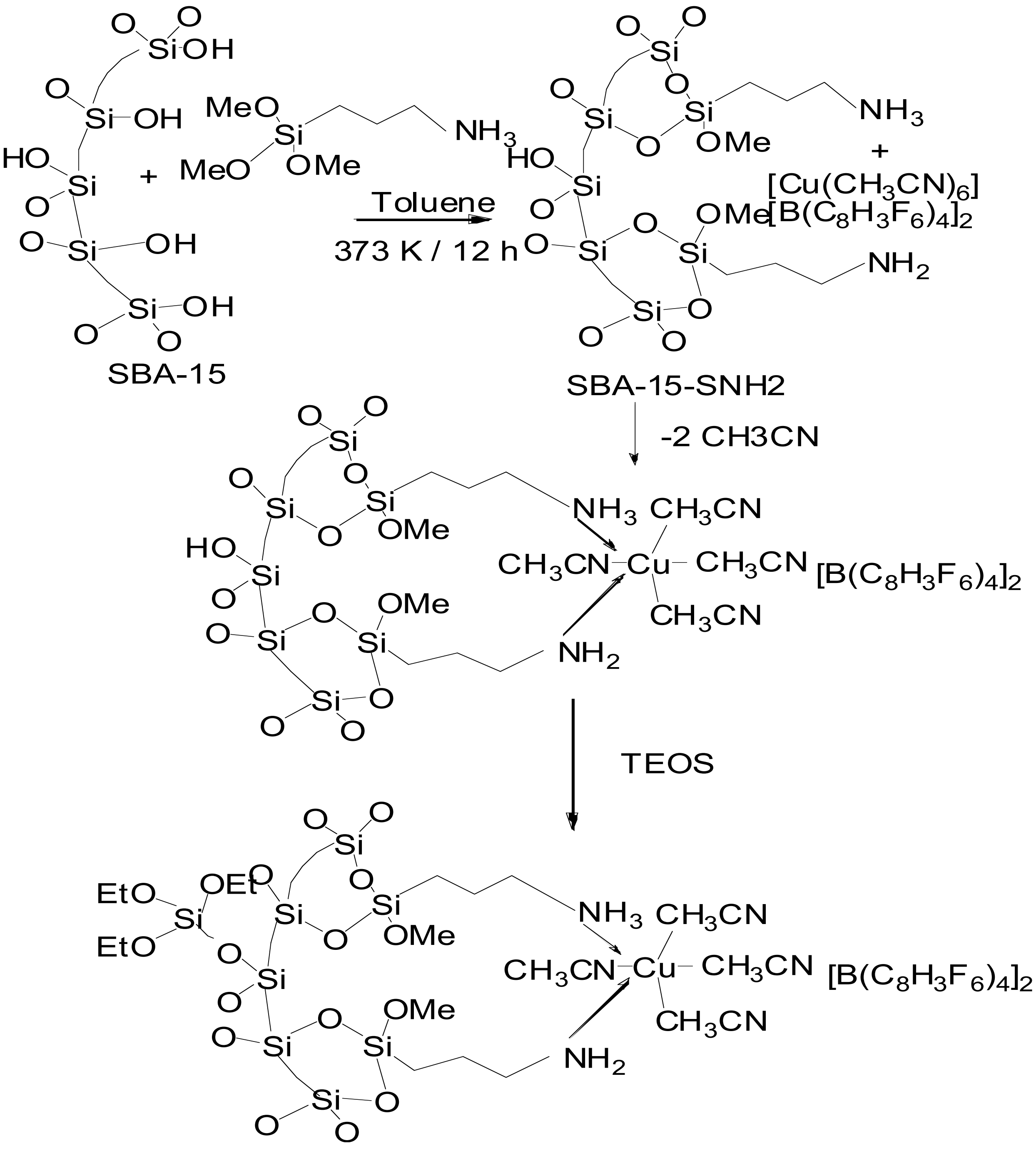
3. Grafting of $[Cu(NCCH_3)_6]$ $[B\{C_6H_3(m\text{-}CF_3)_2\}_4]_2$ on the surface of aminosilane modified SBA-15

3.1. Background

The olefination of aldehydes and ketones is an important transformation in organic synthesis, since the formation of a carbon-carbon double bond is one of the most convenient and universal methods for the preparation of alkenes. [1] Although the Wittig reaction and its modifications [2] are highly effective and general methods, they still have several drawbacks such as the low selectivity for some ylides, the possible epimerization of base-sensitive substrates and the involvement of multi-step processes. [3, 4] Some of the applied reaction systems are employing stoichiometric organometallic reagents, such as those based on titanium and zinc. [5] However, the use of stoichiometric amounts of metal containing systems is an undesired factor indicating that there is still a significant need to develop better reagents to carry out Wittig type reactions. A particularly favourable way to utilize organometallic reagents to improve or enable aldehyde or ketone olefination reactions is the use of such reagents as catalysts. [6]

Huang et al. presented a one pot reaction of tributylstibine, diazocompounds, carbonyl compounds (including both aldehydes and ketones) and a catalytic amount of Cu(I)I, leading to olefin yields of up to 98 % within 4 h reaction time at reaction temperatures of 40 – 80 °C. About 5 – 20 mol% catalyst have been used for this transformation. Stibonium ylides are formed as intermediates. Several other Cu compounds representing formal Cu oxidation states between 0 and II have been examined. The most efficient catalyst was found to be Cu(I)I. [7] In a continuation of this work Huang et al. demonstrated that a one pot reaction of diorganyl telluride, diazocompounds and carbonyl compounds (including again both aldehydes and ketones) and a catalytic amount of Cu(I)I affords the olefination products in yields of up to 95 %, in *E*-configuration, at a reaction temperature of 100 °C within 5 h. The CuI catalyst was used in an amount of 30 mol%. Other Cu complexes lead to lower product yields. [8] Nenaidenko et al. reported in a series of papers on a related catalytic olefination reaction of aromatic aldehydes and ketones. [9] They found that N-unsubstituted hydrazones of aromatic carbonyl compounds can be transformed into the corresponding substituted alkenes by treatment with polyhalogenated alkanes in the presence of catalytic amounts (10 mol %) of CuCl. Here, Cu(I) is oxidized to Cu(II), which is then used in the production of the alkene. [9h]

Transition metal complexes with weakly or non coordinating anions (WCA) are of significant interest both in synthesis and catalysis. [10] For example, a series of acetonitrile complexes of the type $[M(NCCH_3)_6][X]_2$ and $[M_2(NCCH_3)_{8-10}][X]_4$ where X = BF_4^-, $B(C_6F_5)_4^-$, $B\{C_6H_3(m\text{-}CF_3)_2\}_4^-$, $((C_6F_5)_3B\text{-}C_3H_3N_2\text{-}B(C_6F_5)_3)^-$ have been described exhibiting excellent activities for the polymerization of cyclopentadiene, methyl cyclopentadiene and in some cases of isobutene in homogeneous phase. [11] Several of these compounds have been heterogenized by Gonçalves *et al.* and by McCann *et al*. The observed catalytic activities, however, were reported to be much lower than in homogeneous phase. [12] Recently, we reported on homogeneous aziridination reactions catalyzed by $[Cu(NCCH_3)_{2-4}][X]_2$. [13] Application of the above mentioned Cu(II) complexes as catalysts for the aldehydes olefination may also be interesting in heterogeneous media due to the generally easier catalyst/product separation procedure in heterogeneous catalysis. Therefore, the heterogenization of selective and defined homogeneous catalysts may allow the combination of the advantages of both homogeneous and heterogeneous catalysts. Among the various supporting materials available, the recently developed mesoporous silicate known as SBA-15 [14] with a regular pore size, a large surface area, a large number of surface silanol groups, and a high chemical and thermal stability, is a very promising candidate as a catalyst support. [15, 16] As already indicated above, the polymerization activity of the previously examined $[M(NCCH_3)_6][X]_2$ systems drops strongly after heterogenization, when the heterogenization involves a reaction of the cation with the surface or surface fixed donor ligands, due to the resulting reduction of the Lewis-acidity. [17] However, it was shown that such an acetonitrile complex can be stabilized on the surface through a bi-dentate pyrazolylpyridine ligand. [17a] Recently several organometallic complexes such as ruthenium phorphyrins, cobalt salen derivatives, and organo-functionalized copper and iron complexes have been immobilized successfully through aminosilane linkers and were applied for catalytic reactions.[18, 19]



$SBA\text{-}15\text{-}SNH_2\text{-}CuX_2$

Scheme 3.1

In the present work, the copper complex $[Cu(NCCH_3)_6]$ $[B\{C_6H_3(m\text{-}CF_3)_2\}_4]_2$ (**1**) is grafted on the surface of aminosilane modified SBA-15 molecular sieves. The homogeneous complex **1** and its heterogenized congener are applied for various aldehyde olefinations of aromatic substrates, in order to compare the activity of the homogeneous and the heterogeneous copper complexes with respect to their catalytic performance.

3.2. Results and discussion

3.2.1. Synthesis and textural characterization

$[Cu(NCCH_3)_6]$ $[B\{C_6H_3(m\text{-}CF_3)_2\}_4]_2$ (**1**) was synthesized as described in the experimrntal section. The observed IR, EPR and EA data confirm that the compound is pure. The Heterogenization of the compound was carried out as depicted in scheme 3.1 (for details see experiment part). The low angle powder XRD patterns of the parent SBA-15 and of the sample grafted with Cu complex (SBA-15-SNH_2-CuX_2) are depicted in Fig. 5.1. Fig. 3.1a shows the XRD pattern of SBA-15, where the main reflection (1 0 0) corresponding to a hexagonal unit cell [14,15] is observed at a 2θ angle of 0.84°, and two other weak reflections are found in the 2θ angle of 1–2°, with an indexing referring to the (1 1 0), and (2 0 0) planes. Fig. 1b shows the XRD pattern of SBA-15-SNH_2-CuX_2, which is also exhibiting a main reflection (1 0 0) corresponding to the (1 0 0) plane, however, compared to parent SBA-15 the grafted sample shows a decrease in the relative intensities and line broadenings of the XRD reflections and there is a clear shift to higher 2θ values. Similar XRD shifts to higher 2θ values were observed by Luo and Lin for Co and Mn salen complexes encapsulated in mesoporous materials. [19a] Nunes *et al.* and Carvalho *et al.* have also reported similar contractions of the XRD angles in mesoporous material grafted with (3-chloropropyl) trimethoxysilane and (3-aminopropyl) trimethoxysilane. [19b, 19c] Thus the observed shift in XRD angles (2θ values) can possibly be attributed to immobilization of organosilane and bulky organometallic groups on the surface of SBA-15 channels. [15a, 19] FT-IR spectra of parent calcined mesoporous SBA-15, aminosilane grafted SBA-15 and of the grafted samples were recorded. The bands at 1206, 1060, and 794 cm^{-1} are attributed to stretching vibrations of the mesoporous framework (Si-O-Si). The presence of a new band in the aminosilane modified and grafted samples (not shown here) in the range of 2853 cm^{-1} is due to C-H stretching vibrations, originating from the CH_2 groups present in the silane ligand. The grafted sample displays two additional new weak bands around 2333 and 2269 cm^{-1}. These bands can be assigned to nitrile (CN) group vibrations of the grafted Cu- compounds. The appearance of bands at 1516, 1470 and 1385 cm^{-1} is due to the $[B\{C_6H_3(m\text{-}CF_3)_2\}_4^-]$ anions. [11] The coordination of an aminosilane with the metal centre of the complex (**1**), replacing two of the acetonitrile ligands was also observed in homogeneous medium (toluene), giving support to the coordination of the aminosilane linker present on the surface to the metal atom by replacing acetonitrile ligands. Elemental analysis (EA) of the grafted sample shows a Cu loading of 0.8 wt. % for SBA-15-SNH_2-CuX_2. A carbon content of 9.2 wt% and a nitrogen content of 2.5 wt% was determined, which is fairly close to the relative weight ratio found in the homogeneous Cu(II) complex.

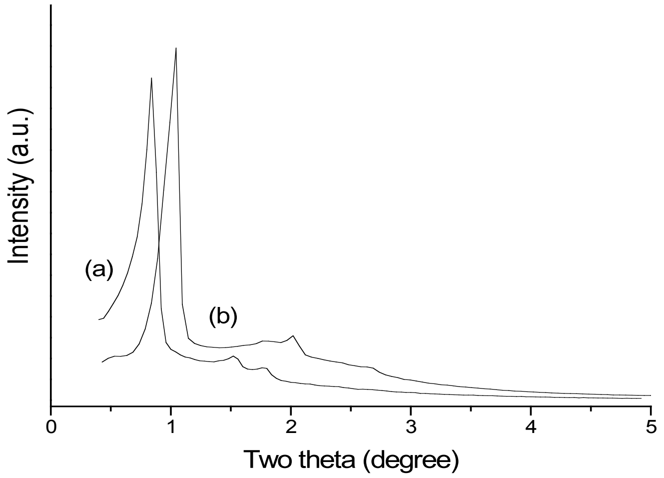


Figure 3.1. XRD pattern of (a) SBA-15, (b) SBA-15-SNH_2-CuX_2.

The low temperature N_2 adsorption/desorption isotherms are of type IV according to the IUPAC [20] and characteristic for mesoporous solids. However, compared to parent mesoporous samples (Fig. 3.2a), the samples bearing grafted Cu complexes (Fig. 3.2b) exhibit a drastic decrease in N_2 uptake due to the relatively high loading with the comparatively bulky organometallic compounds on the surface of the mesoporous channels. Furthermore, the parent SBA-15 sample exhibits a narrow pore size distribution with average pore diameters of 5.4 nm (see inset of Fig 3.2a). The grafted materials show relatively broad pore size distribution with a maximum centred at 5.1 nm (for SBA-15-SNH_2-CuX_2) and display also a decrease in surface area (from 750 m^2 g^{-1} for SBA-15 to 347 m^2 g^{-1} for SBA-15-SNH_2-CuX_2). Furthermore, the pore volume of the grafted samples is reduced to 0.44 cm^3 g^{-1}, compared to 1.1 cm^3 g^{-1} of the parent SBA-15. The decrease of pore volume and the broadening of the pore size distribution evidences that the organometallic complexes and silane linkers in the grafted mesoporous samples are mainly located on the internal surface of the mesoporous material. Similar severe decreases in pore volume and similar broadenings of pore sizes were observed with mesoporous materials grafted with organo silanes and other organometallic molecules. [18, 19, 21] However, the micropore volume (18 %) is not affected much after grafting, which might be due to the difficulty of the comparatively bulky organometallic complexes to access small micropores. The internal and external surface areas of the materials are calculated from the total surface area (from the slope of the initial linear part of the graph). [22] The external surface area of parent material is 41 m^2 g^{-1} and it remains almost the same after the grafting process (38 m^2 g^{-1}), however the internal surface area is 709 m^2 g^{-1} for SBA-15 and is reduced to 309 m^2 g^{-1} for SBA-15-SNH_2-CuX_2 indicating that most of the aminosilane linkers and the copper complexes are grafted on the internal surface of the material. SEM image shows many rope-like domains with a relatively uniform length of 5 μm. These domains are aggregated to a wheat like macrostructure similar to earlier reported morphologies. [14]

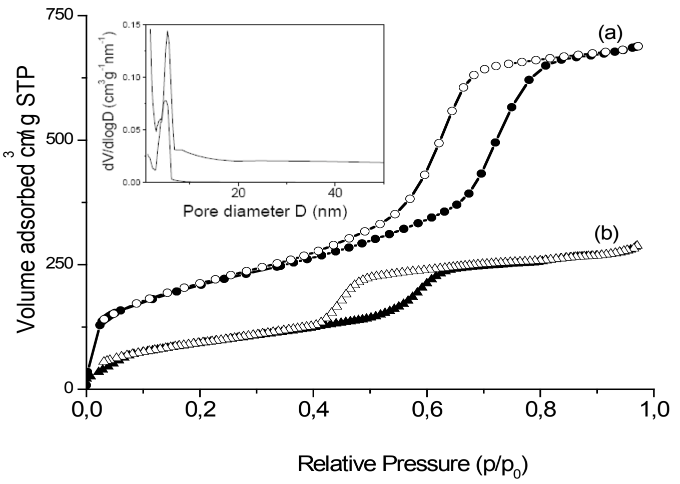


Figure 3.2. N_2 adsorption and desorption analysis of (a) SBA-15 and (b) SBA-15-SNH$_2$-CuX$_2$ (The inset shows the BJH pore size distribution calculated from the desorption branch of the isotherm).

The TEM images (Fig. 3.3) of the grafted samples are providing strong evidence that the mesoporous structure of the support retains long range ordering [15] throughout the grafting process and that the channels remain accessible.

The theoretical value of silanol groups present in SBA-15 materials synthesized under similar conditions is 4x10^{18} Si-OH groups per square meter. [23] From that figure it can be derived that four Si-OH moieties are present per square nanometer. The nitrogen content of the silylated sample is corresponding to the amount of aminosilane linkers present in the sample. Elemental analysis reveals that the nitrogen content of the samples is 2.2 wt. %. Based on these figures the number of aminosilane molecules present in the silylated material is 1.26 per nm^2. This means that about 31 % of the silanol moieties have reacted with the aminosilane linker. Similarly, from the Cu content can be derived that – on average - 0.22 molecules of compound **1** are present per nm^2 of the mesoporous material.

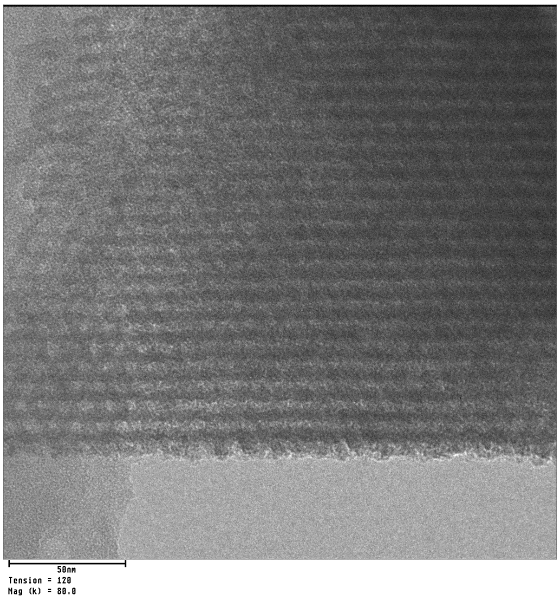


Figure 3.3. TEM images of SBA-15-SNH_2-CuX_2 (insert: electron diffraction pattern).

The parent SBA-15 and the grafted samples were examined by solid-state ^{29}Si CP MAS NMR spectroscopy. The parent SBA-15 (Fig. 3.4a) exhibits two broad elaborate resonances in the ^{29}Si CP MAS NMR spectrum at $\delta = -114.0$ and -102.9 ppm, assigned to Q_4 and Q_3 species of the silica framework, respectively, $[Q_n = Si(OSi)_n(OH)_{4-n}]$. [15] A weak shoulder is also observed at $\delta = -93.5$ ppm for the Q_2 species. The grafting of the copper complex on the mesoporous material results, as expected, in a reduction of the Q_2 and Q_3 resonances (Fig. 3.4b), and a concurrent increase of the Q_4 resonance. The ^{29}Si CP MAS NMR spectrum of SBA-15-SNH_2-CuX_2 (Fig. 3.4b) also exhibits two additional signals at $\delta = -59.9$ and -67.4 ppm being assigned to T_2 and T_3 organosilica species, respectively, $[T_m = RSi(OSi)_m(OR)_{3-m}]$. This is consistent with an esterification of the silanol groups (single and geminal) by nucleophilic substitution at the silicon atom of the organic ligand. [15] However, also as expected, the silylated and the copper complex grafted sample show quite similar ^{29}Si CP MAS NMR signals, thus indicating that after the silylation followed by the grafting process of the Cu compound there is no significant change in the silicon environment. The observed changes in the signals of the ^{29}Si CP MAS NMR spectra arise only during the silylation procedure using 3-aminopropyl silane.

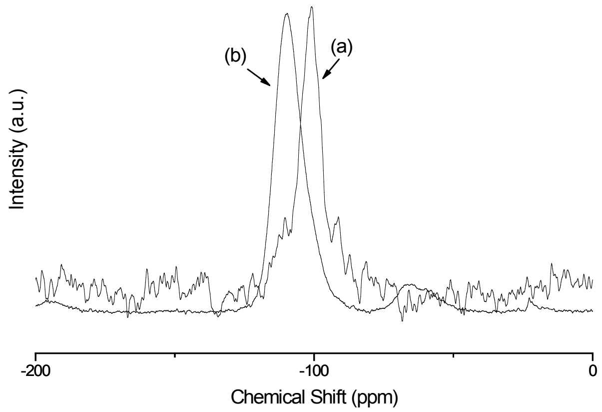


Figure 3.4. ^{29}Si CP MAS NMR spectra of (a) SBA-15 and (b) SBA-15-SNH$_2$-CuX$_2$.

The TG-MS spectrum of SBA-15-SNH$_2$-CuX$_2$ (Fig. 3.5) shows a weight loss of about 14 wt. % up to 1273 K, due to decomposition of the copper acetonitrile complex (**1**) and of the silane linker molecules present in the channels of the mesoporous molecular sieves. The observed mass values associated with $m/z^+ = 14$, 15, 16, 26, 69 and 75 are corresponding to methylene (CH_2), methyl (CH_3), amino (NH_2), cyano (CN), trifluoro methyl (CF_3) and C_6H_3 groups, respectively.

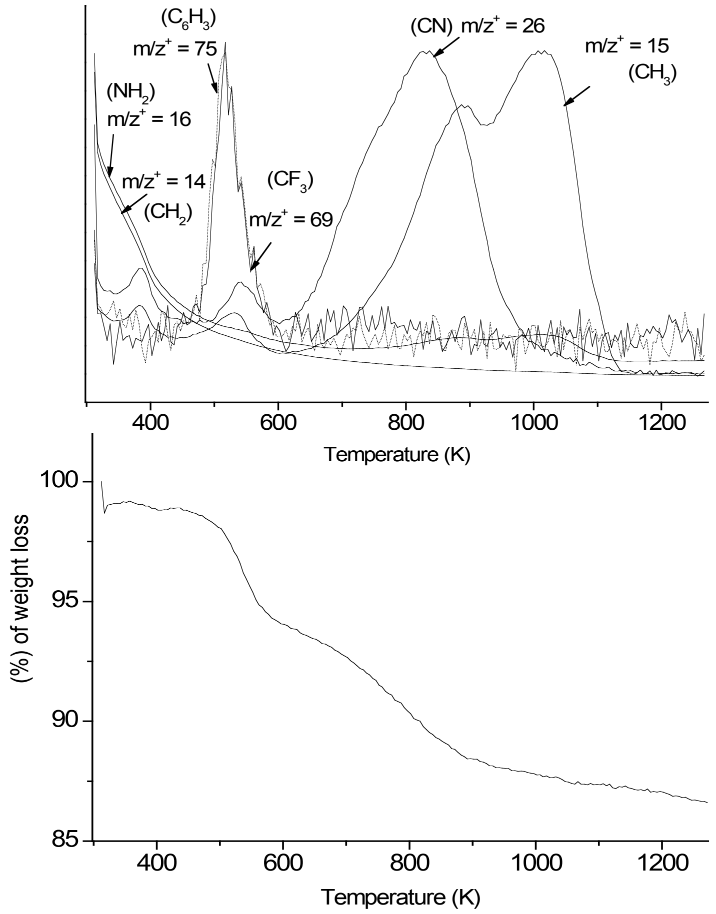
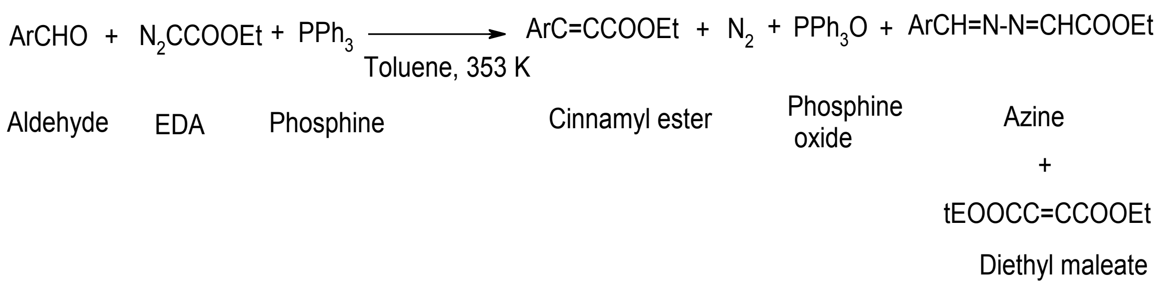


Figure 3.5. TG-MS spectrum of SBA-15-SNH_2-CuX_2.

3.2.2. Catalytic applications

The heterogeneous SBA-15-SNH_2-CuX_2 system is applied for the benzaldehyde olefination (using a 1 : 300 catalyst : benzaldehyde molar ratio, based on the Cu content of the samples), with ethyl diazoacetate (EDA) in the presence of triphenylphosphine. The obtained results are given in Table 3.1. The catalytic reaction shows good conversions and comparable yields during repeated runs. Azine and diethyl maleate are formed as side products (Scheme 3.2).



$$\mathrm{ArCHO} + \mathrm{N_2CCOOEt} + \mathrm{PPh_3} \xrightarrow[\text{Toluene, 353 K}]{} \mathrm{ArC{=}CCOOEt} + \mathrm{N_2} + \mathrm{PPh_3O} + \mathrm{ArCH{=}N{-}N{=}CHCOOEt} + \mathrm{tEOOCC{=}CCOOEt}$$

Scheme 3.2

Fig. 3.6 shows the effect of the reaction time on the conversion of benzaldehyde and on the product yield. About 45 % yield of the desired olefin is obtained, being the major product, with an *E*:*Z* ratio of 90 :10 after 24 h of time. There is a slight decrease of activity from the first to the second run, but the fact that the catalyst remains active for further runs shows that the grafted compounds are stable on the surface. The decrease in catalytic activity between the first and the second catalytic run (8 %) may be due to slight leaching of the weakly bonded copper complexes on the surface of the SBA-15 materials at the reaction temperature (353 K). This assumption is supported by elemental analysis of the residual copper content. In order to examine the extent of leaching on recycled catalyst, control experiments were performed. The catalytic reaction is interrupted after a 50% conversion of the substrate, the solution is filtered off at reaction temperature and the filtrate is examined for its catalytic activity. The lack of Cu in the filtrate solution of subsequent runs, as well as the absence of catalytic conversion in the filtrate show that the catalysts are then stable and leaching is insignificant after the first run. Since there is no appreciable leaching of the catalytic active species, a homogeneous catalysis does not take place and is accordingly not responsible for at least part of the observed catalytic behaviour.

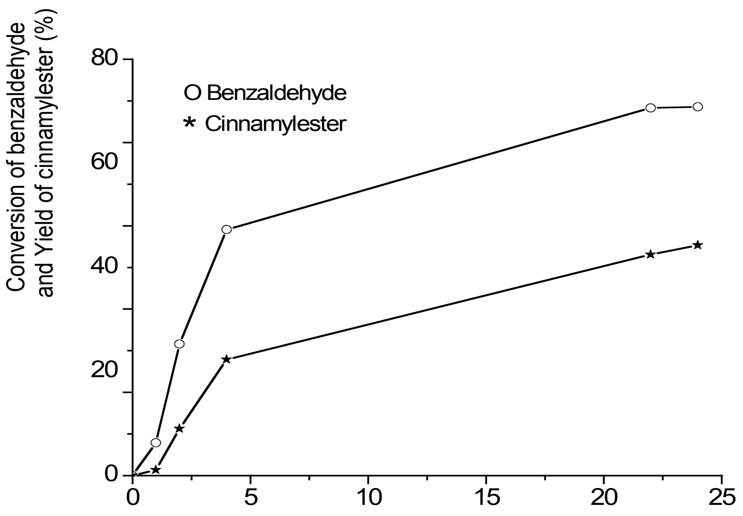


Figure 3.6. Effect of time vs, conversion of benzaldehyde and yield of olefin.

Table 3.1. Benzaldehyde olefination over SBA-15-SNH_2-CuX_2 as catalyst.[†]

Catalyst	Conv. (%)[a]	Sel. (%)[b]	Yield (%)	Ratio of olefin	
				Cis	Trans
SBA-15-SNH_2-CuX_2	70.9	62.4	44.3	9.2	90.8
2nd run	70.9	50.8	36.0	14.0	86.0
3rd run	70.3	50.0	35.1	9.1	90.9

[†] Catalyst : benzaldehyde ratio = 1 : 300; Temperature = 353 K; Time = 24 h.

Molar ratio benzaldehyde : azo compound : Ph_3P = 1.0 : 1.2 : 1.1.

[a] Conv. = Conversion; [b] Sel. = Selectivity.

For comparison, both the homogeneous and heterogeneous catalysts are also tested using two 4-substituted benzaldehydes under identical reaction conditions and the results are summarized in Table 3.2. The obtained results demonstrate that electron donating substituents in 4-position of the phenyl ring enhance catalytic activity both for homogeneous and heterogeneous catalysis due to the easier removal of the oxygen atom. Accordingly, electron withdrawing substitution results in drastic reduction of catalytic activity. The heterogenized catalyst shows better performance than the homogeneous catalyst possibly owing to the uniform distribution and site isolation of active sites on the surface. [21] The isolation of the catalytic sites in the heterogeneous catalyst helps to avoid self-degradation, as it had been observed for the homogeneous catalysts, thus enabling higher catalytic activity in the heterogeneous phase. [21a] This site isolation is indirectly evident from number of copper atoms per nm^2 of mesoporous materials, (see above). Only 20 % of the surface –OH groups is utilized for the immobilization of the Cu catalyst. Such an isolation of the active site obviously helps preventing self-degrading, [21] thus leading to higher yields. Despite being – at least at the first glance – less active than solely homogeneous catalysts described previously by other groups, the catalyst can be reused several times because of the heterogenization. It has to be noted further, that the catalyst amounts applied here are significantly lower than those reported for other Cu based olefination catalysts before. [7-9]

Table 3.2. Olefination of various aldehydes with homogeneous compound **1** and over SBA-15-SNH_2-CuX_2 as the catalyst.[†]

Aldehyde	Compound **1**					SBA-15-SNH_2-CuX_2				
	Conv. (%)[a]	Sel. (%)[b]	Yield (%)	Ratio of olefin		Conv. (%)[a]	Sel. (%)[b]	Yield (%)	Ratio of olefin	
				Cis	Trans				Cis-	Trans-
Benzaldehyde	54.2	22.3	12.1	5.9	94.1	70.9	62.4	44.3	9.2	90.8
4-dimethylamino benzaldehyde	55.1	58.1	32.0	3.1	96.9	75.3	74.1	55.8	5.2	94.8
4-nitro benzaldehyde	50.6	5.6	2.8	---	100	56.1	14.6	8.2	4.1	95.9

[†] Catalyst : Aldehyde ratio = 1 : 300; Temperature = 353 K; Time = 24 h.

Molar ratio benzaldehyde : azo compound : Ph_3P = 1.0 : 1.2 : 1.1.

[a] Conv. = Conversion; [b] Sel. = Selectivity.

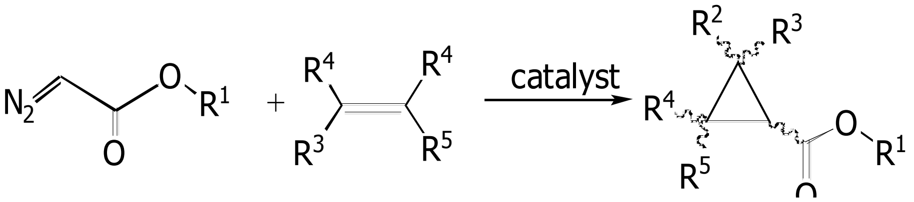
3.3. Conclusion

$[Cu(NCCH_3)_6][B\{C_6H_3(\mathit{m}\text{-}CF_3)_2\}_4]_2$ (**1**) can be successfully heterogenized on the surface of mesoporous SBA-15 molecular sieves by co-ordination via an amino silane linker. The XRD, TEM, and N_2 adsorption isotherms confirm that the surfaces retain long range ordering throughout the grafting process. FT-IR, TG-MS and elemental analyses confirm the successful grafting of the copper complex on the surface. The heterogeneous and homogenous catalysts are found to be of comparable activity for aldehydes olefination reactions. The heterogenized catalyst can be reused for several runs and is applicable in comparatively low amounts.

4. Heterogenization of solvent-ligated copper (II) complexes on poly(4-vinylpyridine) for the catalytic cyclopropanation of olefins

4.1. Background

The use of the cyclopropyl fragment has been widespread and received considerable interest in both chemistry and biochemistry, since cylopropyl moieties are applicable as intermediates in cross-coupling reactions, ring opening reactions and for the synthesis of organic molecules similar to natural products, being used in the production of insecticides and modern pharmaceuticals. The most frequently used method for the preparation of compounds containing the cyclopropyl moiety is the metal-mediated cycloaddition of a carbine fragment to an olefin, the so called cyclopropanation (see Scheme 4.1).[1-4]



Scheme 4.1

In order to further improve such reactions, numerous catalysts, mainly transition metal complexes have been applied in both homogeneous and heterogeneous phase.[5] Copper-based complexes in homogeneous phase are found to play a prominent role for the in situ generation of metal carbenes (or carbenoids) starting from diazo compounds and nitrenes in the homogeneous phase.[6-8]

In this regard, various copper complexes (such as copper bis(oxazoline)s) have been immobilized on the surfaces of zeolites (e. g. zeolite-Y), mesoporous molecular sieves and clays and also on Cu^{2+} exchanged zeolite-Y. Such materials are utilized as heterogeneous catalysts for aziridination and cycloproponation reactions.[9-11] In most cases, immobilization is carried out by covalent binding. The method used to form this covalent bond seems to have decisive influence on the catalytic activity and selectivity.

The development of polymer-supported and insoluble (heterogeneous) transition metal catalysts has attracted a great deal of attention in organic chemistry due to the stability and uniformity of the obtained materials and the possibility of easy product/catalyst separation, combining the advantages of homogeneous and heterogeneous catalysis. Such systems containing immobilized organometallic (catalyst) compounds have several advantages, such as the simple recycling of the catalysts by filtration, which in turn prevents the loss of both ligands and (heavy) metals thus considerably decreasing the environmental problems of waste materials. Several types of linkers, among them (N-heterolytic carbene)-ligands have been designed, to create stable carrier-catalyst interactions.[12]

The use of weakly or non coordinating anions (WCA) as counter ions both in synthesis and catalysis is of significant current interest, due to their potential in enhancing the reactivity of metal complexes.[13] The successful synthesis of a series of acetonitrile complexes of the type $[Mn(NCCH_3)_6][X]_2$ and $[Mo_2(NCCH_3)_{8-10}][X]_4$ where X = BF_4, $B(C_6F_5)_4$, $B\{C_6H_3(m\text{-}CF_3)_2\}_4$, $((C_6F_5)_3B–\ C_3H_3N_2–B(C_6F_5)_3)$, exhibiting excellent activities for the polymerization of cyclopentadiene, methylcyclopentadiene and isobutene, in homogeneous and heterogeneous phase has been reported.[13c, 13d and 14] Some of these latter compounds have been heterogenized by Goncalves et al. and McCann et al. on mesoporous materials and zeolites. The observed catalytic activities, however, were reported to be much lower than in homogeneous phase.[15] In the present work, $[Cu(NCCH_3)_6][B(C_6F_5)_4]_2$ (**1**) and $[Cu(NCCH_3)_6][B\{C_6H_3(CF_3)_2\}_4]_2$ (**2**) are grafted on the surface of P4VP (poly(4-vinylpyridine) to form P4VP-**1** and P4VP-**2**. Both the homogeneous compounds **1** and **2** as well as the immobilized complexes P4VP-1 and P4VP-2 are applied for a variety of olefin cyclopropanation reactions using diazoethlacetate (EDA) and the activities in catalysis are compared. Recently we had reported on the successful heterogenization of $[Cu(NCCH_3)_6][B(C_6F_5)_4]_2$ on NaAlMCM-41 and NaAlMCM-48 and the applictions in catalytic olefin aziridination.[5]

4.2. Results and discussion

4.2.1. Synthesis and textural characterization

$[Cu(NCCH_3)_6][B(C_6F_5)_4]_2$ (**1**) and $[Cu(NCCH_3)_6][B\{C_6H_3(CF_3)_2\}_4]_2$ (**2**) are synthesized as described in the experimental section. The FT-IR, EPR and EA data confirm that the compounds are pure. The obtained copper-loading of the two complexes grafted on P4VP determined by elemental analyses (EA) show that a higher amount of complex **1** is grafted on P4VP (0.9 wt.% Cu) than of complex **2** (0.8 wt.% Cu). The observed higher Cu complex loading in P4VP-**1** might be due to the smaller steric bulk of the anion of complex **1** (in comparison to the anion of complex **2**).

Fig. 4.1 shows the FT-IR spectra of pure P4VP and of the grafted samples. The presence of two new weak bands around 2333 and 2269 cm^{-1} can be observed. These peaks can be assigned to the fundamental ν_2 CN stretching mode and a combination mode ($\nu_3 + \nu_4$) of the acetonitrile ligands of the grafted compounds. The values are identical within the measurement error to that of the homogeneous complexes (2340 and 2279 cm^{-1} for complex **1**, 2332 and 2271 cm^{-1} for complex **2**). Vibrations of free CH_3CN (2293, 2253 cm^{-1}) are not observed in the IR spectra of the products.

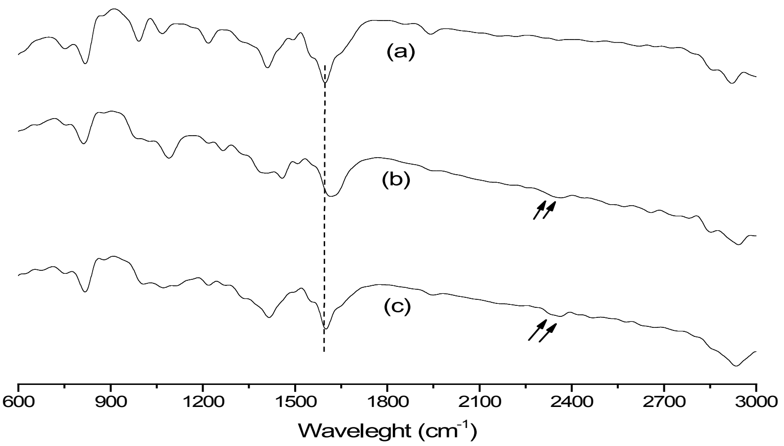
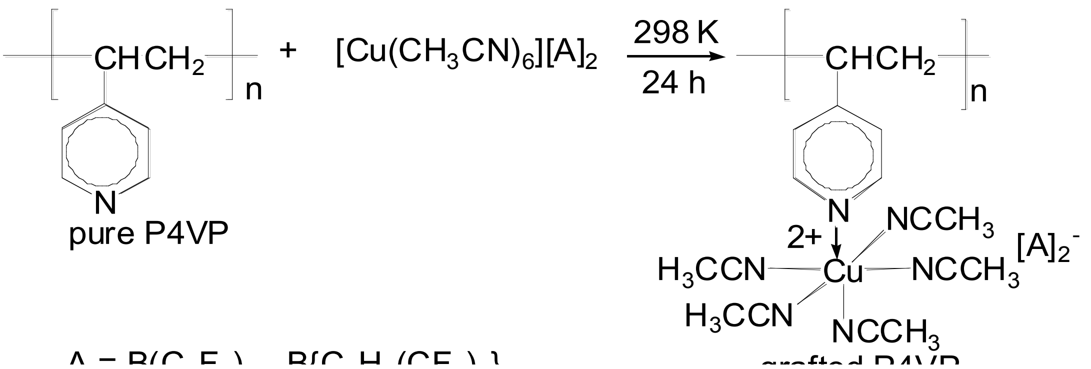


Figure 4.1. FT-IR spectra of (a) the pure P4VP, (b) P4VP-Complex **1** and (c) P4VP-Complex **2**

It also can be seen from the FT-IR spectra that the characteristic stretching vibrations of pyridine rings appear at *ca.* 1600 cm^{-1} for pure P4VP (doted line). However, due to the presence of the coordinated copper (II) ions in the two materials, the vibration mode is shifted to around 1605-1620 cm^{-1} suggesting a donor-acceptor interaction between the pyridine nitrogen atoms and the copper metal [17] as depicted in Scheme 4.2.



Scheme 4.2

Fig. 4.2 shows the TG-MS plot for pure P4VP and for both grafted complexes. The thermogram of pure P4VP (dry) shows a weight loss of 92 % between 330 and 440° C due to the degradation of the polymer, including the destruction of its vinyl backbone and the pyridine rings. For both grafted complexes, the main degradation stage starts at *ca.* 250 ºC and finishes at ca. 470 ºC. The weight loss of P4VP-**1** and P4VP-**2** are 67 and 85% respectively. According to the obtained mass spectra the decomposition starts with the loss of the nitrile ligands and the subsequent degradation of the counter ions, leaving mainly cupper metal and polymer backbone (EA evidence), the latter des-integrating at higher temperatures, but still within the interval given above. Clear separations between these different degradation steps cannot be observed. The mass values obtained by the coupled mass spectroscopy (e.g. $m/z^+ = 26$ and 15 corresponding to nitrile (CN) and methyl (CH_3) groups) are as expected. Also not unexpectedly, the grafted complexes are less thermally stable than the pure P4VP carrier material.[16]

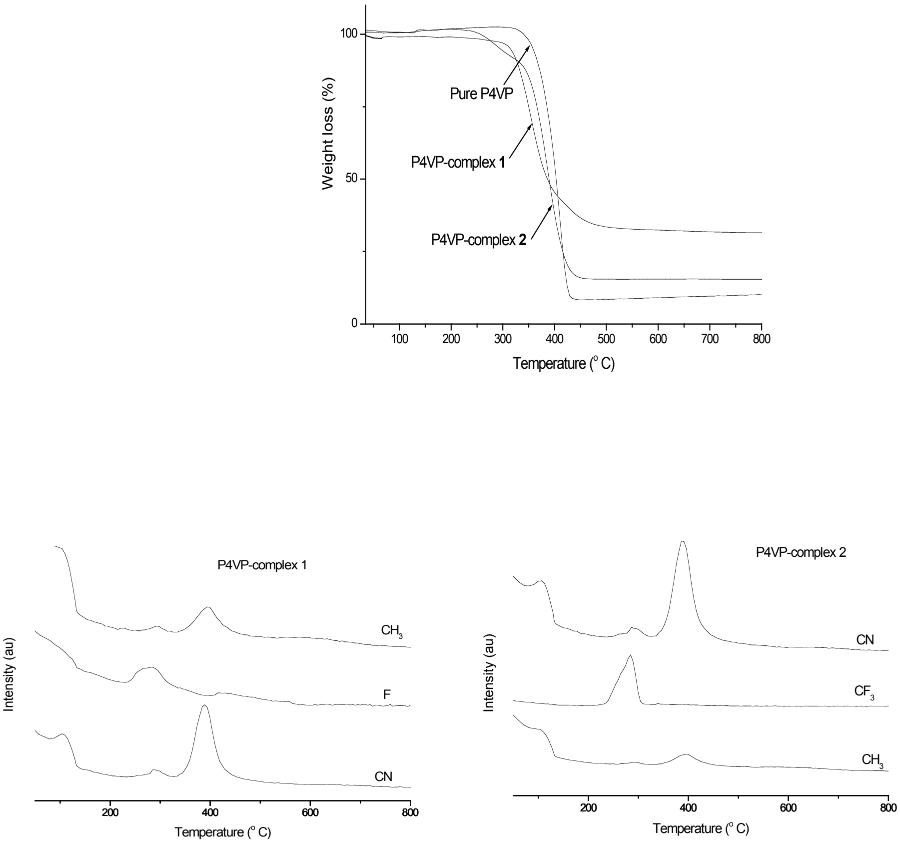


Figure 4.2. TG-MS plot of pure P4VP, P4VP-Complex **1** and P4VP-Complex **2**

However, the decomposition behaviour of compounds **1** and **2** (not depicted) is significantly different. Complex **1** shows its first decomposition onset already at 167°C, being the mass loss ca. 14 %. Since an analogous decomposition step can not be found in acetonitrile free K[B(C_6F_5)$_4$], it must correspond to the loss of all six acetonitrile ligands, amounting to 14.7% of the total mass of compound **1**. The second and last decomposition step starts at 235°C and corresponds to a mass loss of ca. 65 % of the original mass. Since K[B(C_6F_5)$_4$] shows a mass loss of 50 % starting at approximately the same temperature, it seems reasonable to argue that this decomposition step accounts for anion fragmentation. Compound **2** shows the lowest thermal stability among all compounds under study and decomposes also in two steps. The first decomposition step occurs at 89 °C and accounts for a ca. 38% mass loss. This step accounts for the loss of all acetonitrile ligands (12%) and additionally anion fragmentation. To the second onset at 165°C corresponds a mass loss of ca. 48% from anion fragmentation. The mass loss is completed at 270°C with a residual value of 9.9%. These observations show the significant stability increase gained by immobilization of compounds **1** and **2**.

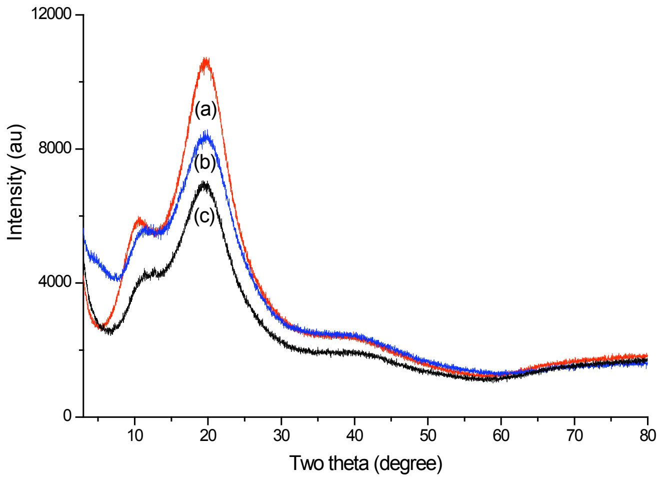


Figure 4.3. Powder X-ray diffraction pattern of (a) pure P4VP, (b) P4VP-Complex **1** and (c) P4VP-Complex **2**.

The powder X-ray pattern of both grafted complexes indicate that the structure of the polymer remains intact throughout the grafting procedure with a decrease of peak intensities compared to pure P4VP (see Fig. 4.3). This change may be due to the contraction of the long chain three dimensional structure of the polymer backbone of grafted P4VP. Complex **1** and **2** are paramagnetic, thus EPR spectra of the grafted samples have been recorded (Fig. 4.4). These spectra are typical for Cu(II) systems ($3d^9$, s=1/2) with strongly distorted octahedral coordination as expected for Cu(II) according to a Jahn-Teller effect and the two different types of ligands (five acetonitriles and one pyridine). The g values (g_{11} = 2.371 ; $g\perp = 2.075$)..are identical for both samples within experimental error. These results further supports the heterogenization of complexes **1** and **2** on P4VP.

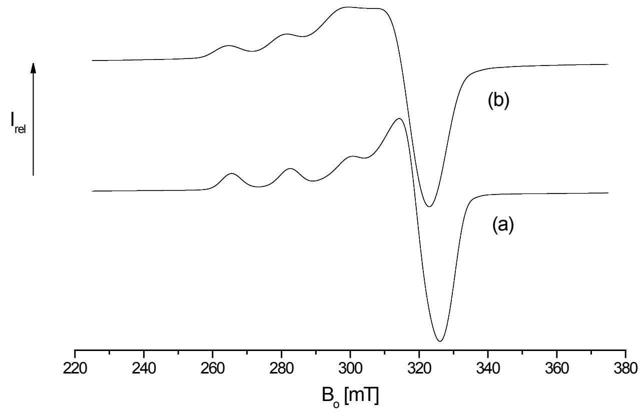


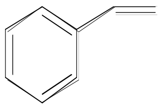
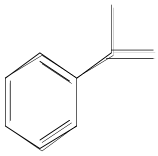
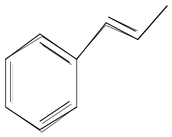
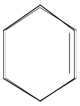
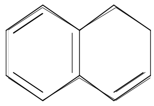
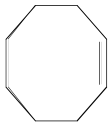
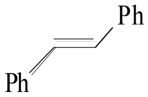
Figure 4.4. EPR spectra of (a) P4VP-Complex 1 and (b) P4VP-Complex 2

4.2.2. Catalytic applications

The catalytic activity of both P4VP-Complex **1** and P4VP-Complex **2** materials were examined in the cyclopropanation of different olefins with EDA at room temperature and then have been compared to their homogeneous congeners as displayed in table 4.1. The grafted polymers show – on average - a somewhat lower activity in the cyclopropanation of olefins than the homogeneous compounds **1** and **2**.

When adding one equivalent of pyridine to a dichlorometahne solution of complex **2**, one of the nitrile ligands is easily replaced by pyridine, as can be concluded from NMR and FT-IR examinations of the products. The resulting complex **2a** can be also applied successfully for olefin cyclopropanation in homogeneous phase, with conversions being *ca.* 20% lower than that obtained with complex **2**. These results show the negative effect of replacing an acetonitrile ligand by the more strongly coordinating pyridine. The three-dimensional and the long chain structure of P4VP, however, seems to play an important role for the catalytic behaviour of both grafted materials and providing a molecule trap, which is beneficial to maintain the interaction between the substrates and the active site of the catalysts (copper (II) ion), as seen in the better results obtained with P4VP-**2** when compared to the homogeneous **2a** (on average *ca.* 5 – 10%). P4VP-**2** as the catalyst leads in most cases to a better yield and seems to be more active for the catalytic reaction than P4VP-**1**. The same observation is made, when applying the non-immobilized compounds **1** and **2**. The effect seems therefore ascribable to the counter anion.

Tabel 4.1. Cyclopropanation of various olefins using EDA with heterogeneous complexes P4VP-Complex **1** and P4VP-Complex **2** and homogeneous complexes **1** and **2**[a]

	Yield (%)[b] and E-selectivity (cis:trans)[c]			
Olefins	P4VP-CuC$_6$F$_5$	P4VP-CuCF$_3$	Complex 1	Complex 2
	29% (38:62)	32% (35:65)	46% (44:66)	53% (36:64)
	17%(17:83)	35% (10:90)	36% (46:54)	43% (47:53)
	16% (23:77)	26% (23:77)	22% (44:66)	33% (42:68)
	48% (23:77)	36 (30:70)	55% (26:74)	59% (29:71)
	10% (36:64)	12% (40:60)	30% (26:74)	44% (30:70)
	58% (7:93)	63%(7:93)	37% (35:65)	48% (32:68)
	11% (0:100)	25% (0:100)	21% (0:100)	27% (0:100)

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[a]Catalyst:Olefins = 1 : 250; [b]Based on EDA conversion; [c]GC-MS; Temperature = 298 K; Reaction time = 24 h.

Tabel 4.2. Cyclopropanation of cyclooctene over various catalysts using EDA[a].

Catalysts	Run	Yield (%)
Poly-Complex **1**	1st run	58
	2nd run	56
	3rd run	30
	4nd run	20
	5rd run	18
Poly-Complex **2**	1st run	63
	2nd run	59
	3rd run	28
	4nd run	22
	5rd run	23

[a] Catalyst : Olefins = 1 : 250; [b] Based on EDA conversion; Temperature = 298 K. Reaction time = 24 h

The catalytic activity of both heterogenized complexes was examined for several runs in the cyclopropanation of cyclooctene. There is an obvious decrease of activity from the second until the fifth run, both for P4VP-**1** and P4VP-**2** (Table 4.2). The occurrence of leaching has been tested by means of elemental analyses, finding the copper loading for both grafted materials after the first run being slightly lower. The filtered solution shows product yields of 2-6 % formed after the separation from the catalyst carrier materials. Leaching of active catalyst is therefore not particularly pronounced and the observed decrease in activity during the recycling experiments may be partially due to adsorption of reactant/product molecules on the polymer or, to a minor extent, to the loss of deactivated (inactive) Cu-containing decomposition products. The Cu-pyridine interaction is stronger than the Cu-nitrile interaction, however, it still is a donor-acceptor interaction, being generally weaker than (most) chemical bonds.

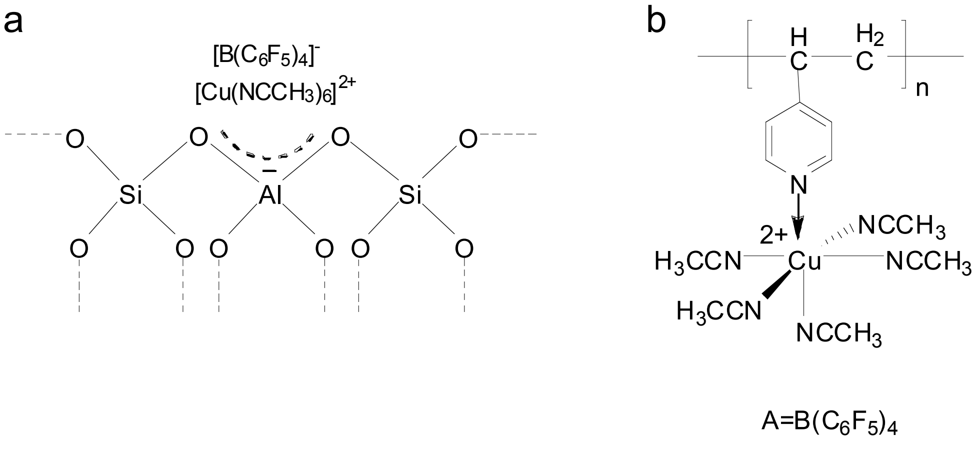
4.3. Conclusion

$[Cu(NCCH_3)_6][B(C_6F_5)_4]_2$ and $[Cu(NCCH_3)_6][B\{C_6H_3(CF_3)_2\}_4]_2$ compounds are successfully grafted on poly(4-vinylpyridine). The homogeneous and heterogeneous catalysts are found to be of comparable activity for the cyclopropanation of olefins. Furthermore, the heterogeneous catalysts remain active and stable for several catalytic runs, although the activity decreases throughout several cycles. An aim for future work will be the generation of a covalent linker-metal bond, which, however, should not reduce the charge of the catalyst cation. We had already shown previously, however, that non immobilized Cu(I) catalysts can also be applied as cyclopropanation catalysts in homogeneous phase.[17]

5. Modified MCM41-Supported Acetonitrile Ligated Copper(II) and Its Catalytic Activity in Cyclopropanation of Olefins

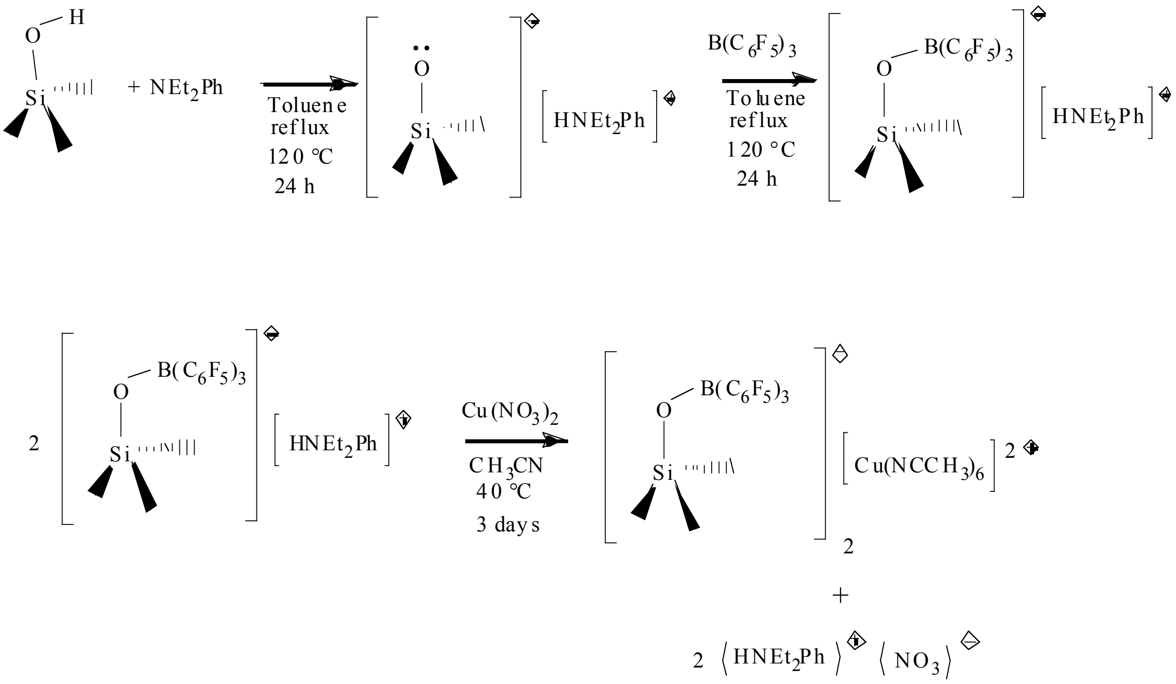
5.1. Background

The use of weakly or non coordinating anions (WCA) as counter ions both in synthesis and catalysis is of significant interest, due to their potential in enhancing the reactivity of metal complexes [1-3]. During the last three decades, a plethora of weakly coordinating anions has been synthesised. In order to produce ever more weakly coordinating anions, the negative charge is usually delocalized over a larger area of non-nucleophilic and chemically robust moieties [4]. A series of acetonitrile complexes of the type $[M(II)(NCCH_3)_6][X]_2$ where X is a WCA, e. g. BF_4, $B(C_6F_5)_4$, $B\{C_6H_3(m\text{-}CF_3)_2\}_4$ and $((C_6F_5)_3B–C_3H_3N_2–B(C_6F_5)_3)$, has been successfully synthesized and applied as catalysts in both homogeneous and heterogeneous phases [1,2,5].



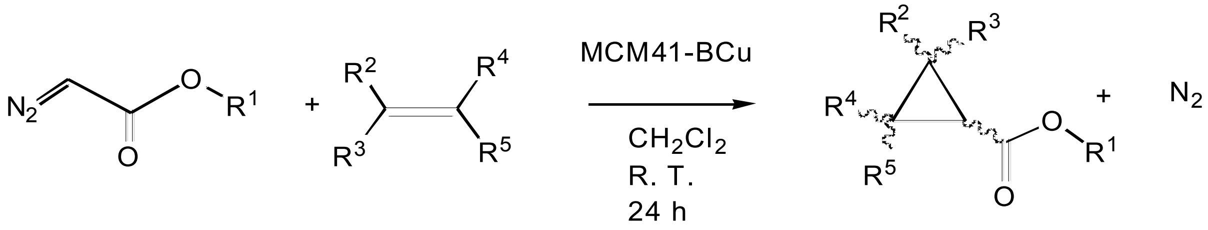
Scheme 5.1. The grafting of $[Cu(NCCH_3)_6][B(C_6F_5)_4]_2$ on AlMCM41/48 (a) and the poly(4-vinylpyridine) (b)

Since copper-based complexes in homogeneous phase are found to play a prominent role for the in situ generation of metal carbenes (or carbenoids) starting from diazo compounds and nitrenes in the homogeneous phase,[6-8] quite some work has been dedicated to such systems,[9-11] For example, homogeneous and immobilized (on mesoporous molecular sieves; i.e. AlMCM41/48 and the polymer poly(4-vinylpyridine)) derivatives of $[Cu(NCCH_3)_6][B(C_6F_5)_4]_2$ have been examined and found to be active in the aziridination and cyclopropanation of various olefins at room temperature [12,13]. Immobilized $[Cu(NCCH_3)_6][B(C_6F_5)_4]_2$ on AlMCM41/48 was ionically grafted while it was covalent anchored on poly(4-vinylpyridine) as illustrated in Scheme 5.1. These techniques of immobilization, however, have some drawbacks, being reflected in some cases in a lower catalytic activity of the immobilized catalysts in comparison to their heterogeneous counterparts. Cation immobilization on a surface can reduce its Lewis acidity considerably and at the same time make the accessibility for a substrate more difficult. Both changes lead to a reduced catalytic activity. Formally replacing one of the non coordinating anions by a negative charge on the surface usually has a similar effect, due to the good donor capabilities of surface $–O^-$ groups and comparatively narrow pores of MCM41 materials. A somewhat different approach, which is seemingly more promising, would be the immobilization of one or two of the counter anions, leaving the cation not bonded to the surface except by cation / anion interactions. Such an anion modified silica surface can be obtained by treating the silica surface first with a strong Lewis acid (i.e. BF_3, $B(C_6F_5)_3$, etc.) in the presence of the Brønsted base NEt_2Ph. Several modifications are then possible to create the desired cation associated with the surface fixed non coordinating anion [14,15].



Scheme 5.2. Synthesis route to acetonitrile ligated copper(II) cations on modified MCM41

In the present work, the cationic complex $[Cu(NCCH_3)_6]^{2+}$ is connected to the surface via an electronic interaction with the surface attached counter ion $-B(C_6F_5)_3^-$ (Scheme 5.2). The obtained grafted materials were systematically characterized by powder X-ray diffraction (XRD), thermogravimetry coupled with mass spectroscopy (TG-MS), Transmission Electron Microscopy (TEM) and FT-IR spectroscopy. The resulting material prepared from modified MCM41 sample is designated as MCM41-BCu. This newly synthesized catalyst and the homogeneous $[Cu(NCCH_3)_6][B(C_6F_5)_4]_2$ are applied for various olefin cyclopropanation reactions using diazoethylacetate (Scheme 5.3), in order to compare the activity of the homogeneous and the heterogeneous copper complexes with respect to their catalytic performance.



Scheme 5.3. General equation for olefin cyclopropanation in dichloromethane

5.2. Results and discussion

5.2.1. Synthesis and textural characterization

Fig. 5.1 depicts the FT-IR spectra of parent mesoporous MCM41 and the grafted sample. The bands at 1206, 1060, and 794 cm^{-1} are attributed to stretching vibrations of the mesoporous framework (Si-O-Si). The band at ca. 960 cm^{-1} is assigned to a vibration mode of the silanol (Si-OH) groups in the mesoporous channels. Sharp bands between 2200 and 2500 cm^{-1} can be assigned to nitrile (CN) group vibrations of the grafted compounds. Free acetonitrile, however, is not present in the spectra. The ν(CN) vibrations of free $NCCH_3$ would be expected at 2253 and 2293 cm^{-1}. Due to the weak coordination of acetonitrile as a ligand to the copper metal center these two peaks are shifted to 2263 and 2299 cm^{-1}. The heterogenization procedure presented here does, therefore, not alter the octahedral coordination sphere of the cation. A very sharp band appears at ca. 1380 cm^{-1}, originating from the $B(C_6F_5)_3$ groups on the surface of MCM41. It is also can be seen that the silanol groups on the channel walls of MCM41 were largely consumed during the heterogenization of the $-B(C_6F_5)_3^-$ moieties.

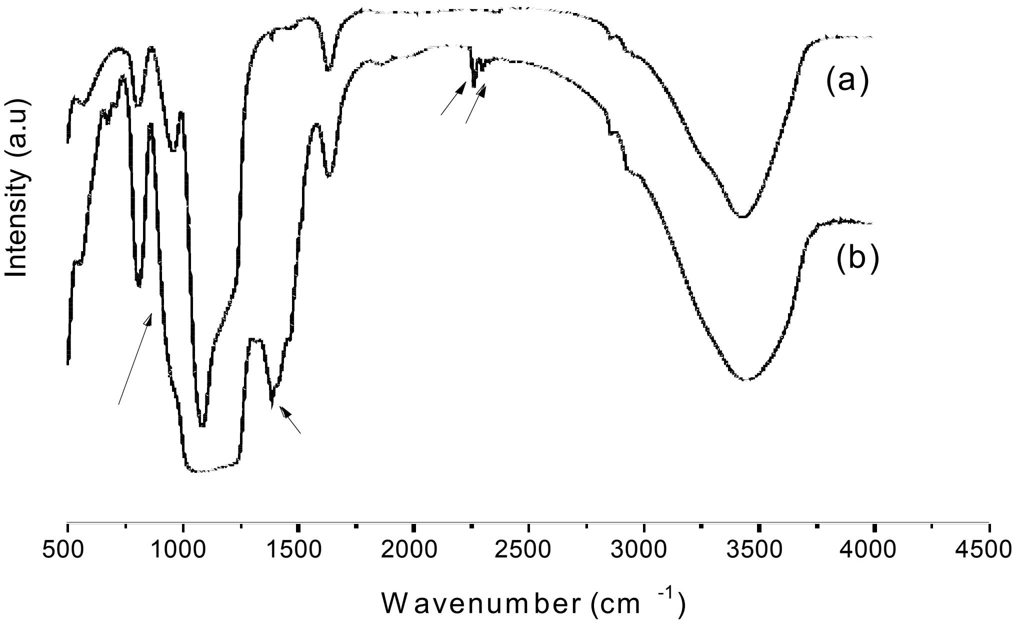


Figure 5.1. The FTIR spectra of parent MCM41(a) and MCM41-BCu (b)

The powder XRD pattern of the parent MCM-sample is in full agreement with the previously reported pattern, indicating the sample to be well ordered (Fig. 5.2).[18,19] Several distinct Bragg peaks are observed in the $2\theta = 2\text{-}8^{\circ}$ region, which can be indexed to the different hkl reflections for a hexagonal unit cell (using the strongest reflection, d_{100}). Even after modifying bulky $B(C_6F_5)_3$ and grafting the cationic complex $[Cu(NCCH_3)_6]^{2+}$ on mesoporous surfaces the higher 2θ peaks are still observed, indicating the retention of the long-range hexagonal symmetry. Compared to parent MCM41 the grafted sample show a decrease in the relative intensities and a broadening of the XRD reflection. There is also a slight shift to higher 2θ values. These changes originate from the immobilization of the complexes inside the channels of MCM41.[18,19]

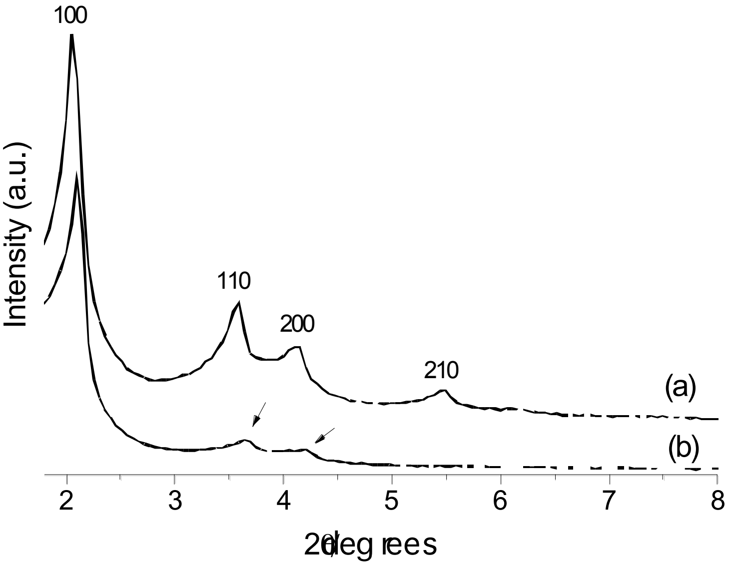


Figure 5.2. Powder-XRD pattern of parent MCM41 (a) and MCM41-BCu (b)

Thermally, the MCM41-BCu is moderately stabile as depicted in Fig. 5.3. The TG-MS spectrum of MCM41-BCu shows about 30 % weight loss up to 1000 °C, the first decomposition onset appearing at 106.4 °C. Since an analogous decomposition step can not be found in acetonitrile free $K[B(C_6F_5)_4]$, it must correspond to the loss of the acetonitrile ligands and according to its magnitude, to additionally anion fragmentation. This observaton limits the application of MCM41-BCu as heterogeneous catalyst to temperatures below 100 °C. The observed mass values $m/z^+ = 26$, 15 and 31 are corresponding to a cyano methyl and CF groups and confirm the presence of the Cu-complexes and anionic $[>Si-B(C_6F_5)_3]$ in the mesoporous channels.

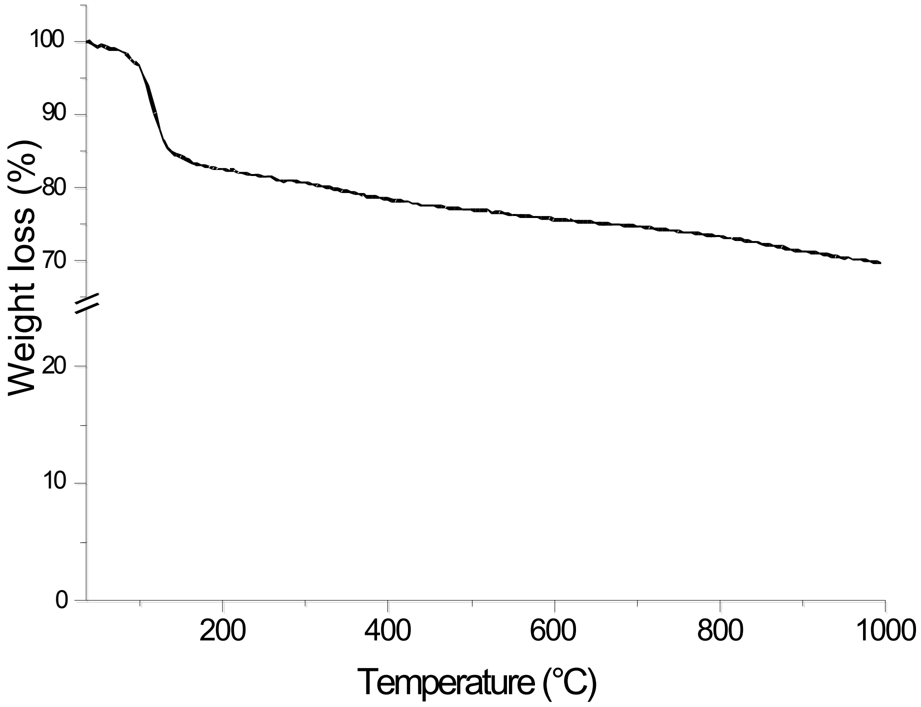


Figure 5.3. TG profile of MCM41-BCu

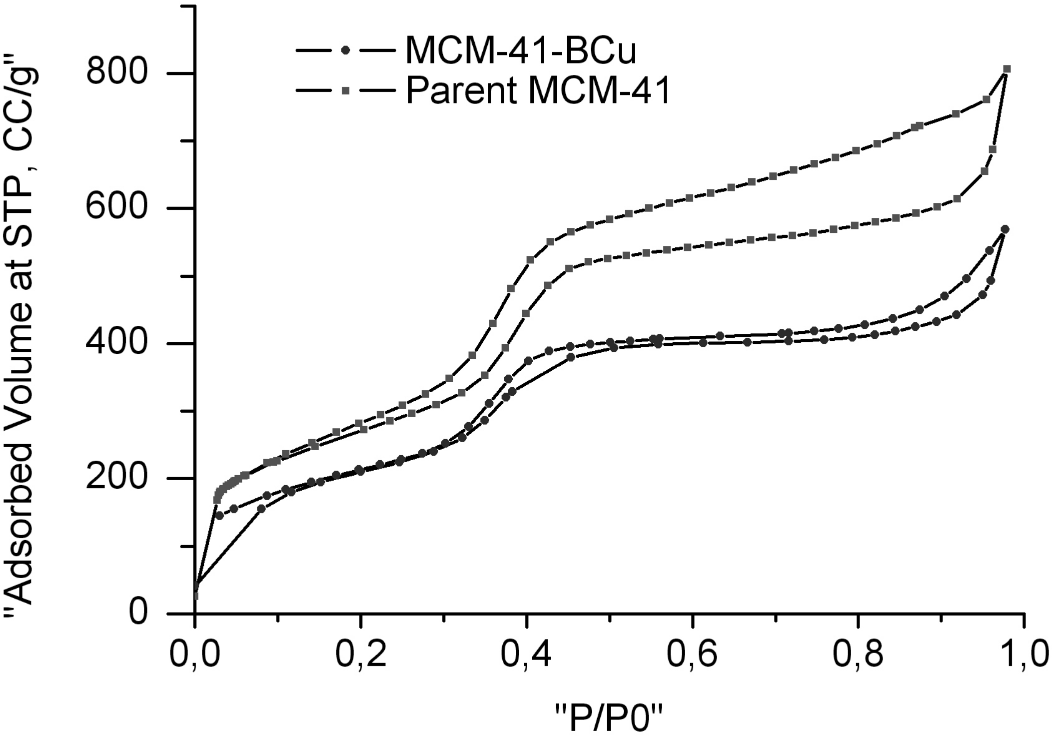
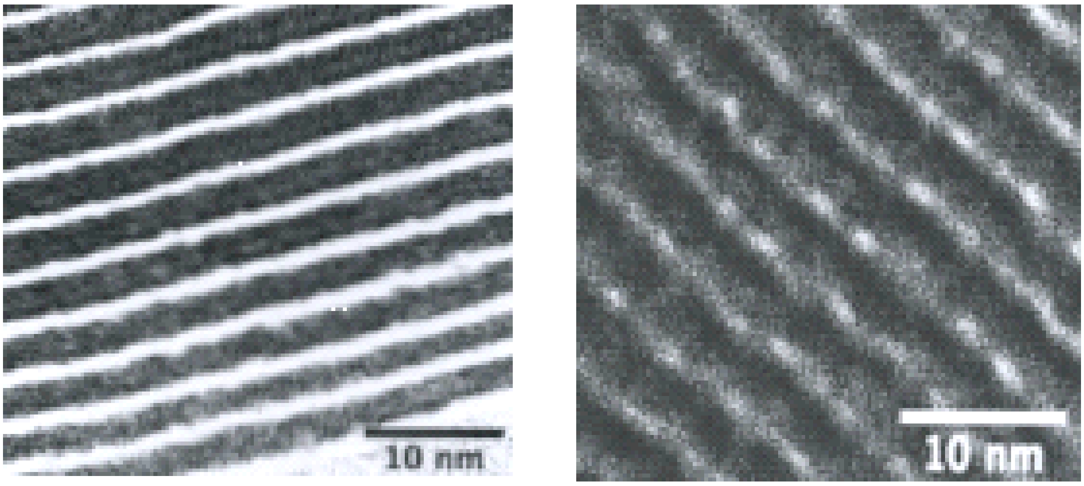


Figure 5.4. BET measurements of parent MCM41 and MCM41-BCu

The success of the grafting process of the catalyst is proven by BET measurements (Fig. 5.4). The obvious differences between the shapes of the BET curves of the parent MCM41 and the grafted sample show that the surfaces and the pores were partially occupied by the grafted catalyst. The BET measurements also provide evidence that the channels of the mesoporous support still remain accessible throughout the grafting process [19, 20]. The uniform TEM images of the grafted sample (Fig. 5.5) show the long range ordering of the support and evidence the structural intactness of the obtained material.



(a) (b)

Figure 5.5. TEM images of parent MCM41 (a) and MCM41-BCu (b)

The grafted sample was measured by solid-state ^{29}Si CP MAS NMR spectroscopy and the result is depicted in Fig. 5.6. The immobilization of the counter anion on the modified mesoporous material by replacing terminal surface –OH groups by -OB$(C_6F_5)_3$ moieties shows as expected a reduction of Q_3 resonances at $\delta = -103.9$ and a concurrent increase of the Q_4 resonance at $\delta = -109.8$ in comparison to the parent sample (not depicted). This fact together with the FTIR and ^{1}H CP MAS NMR results evidences the formation of [>Si-OB$(C_6F_5)_3]_2[Cu(NCCH_3)_6]$ species. A weak shoulder is also observed at $\delta = -90.7$ ppm for the Q_2 species.

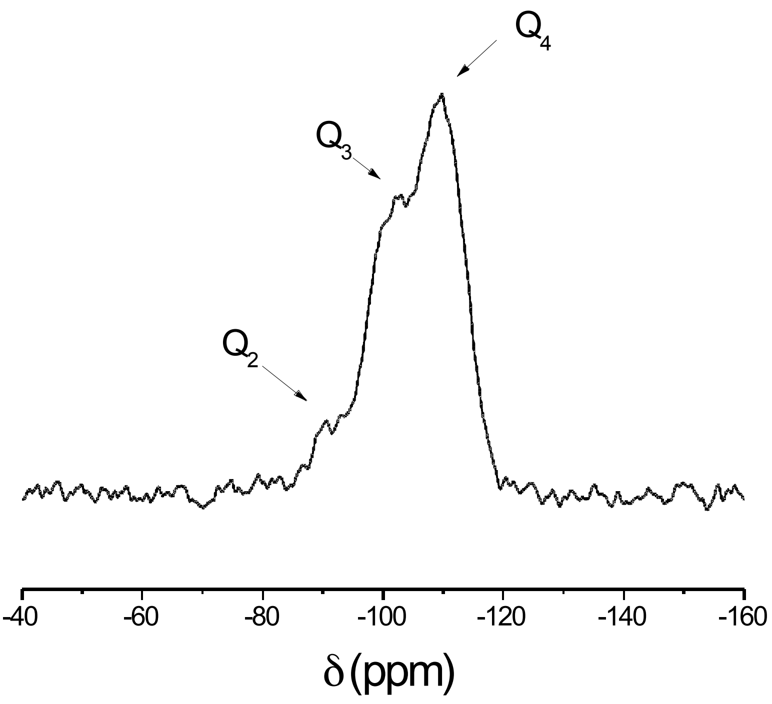
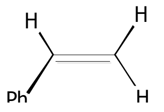
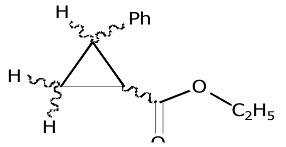
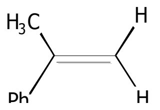
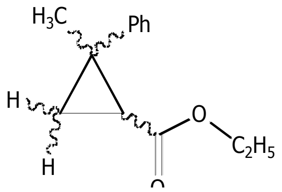
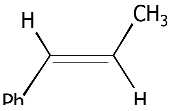
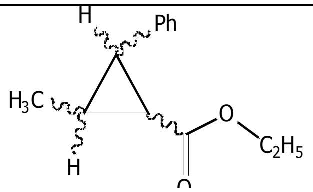
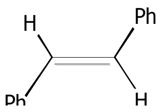
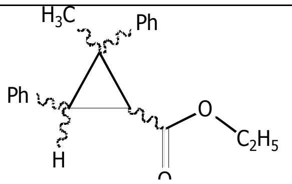
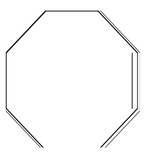
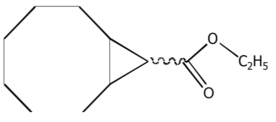


Figure 5.6. ^{29}Si MAS NMR spectra of MCM41-BCu recorded at 5 kHz

5.2.2 Catalytic applications

The heterogeneous MCM41-BCu sample and $[Cu(NCCH_3)_6][B(C_6F_5)_4]_2$ were applied as catalysts for olefin cyclopropanation reactions (Scheme. 3) using ethyl diazoacetate (EDA) at room temperature as summarized in Table 5.1. The heterogeneous catalyst shows lower product yields than the homogeneous catalyst. Due to high reactivity of such copper complexes many side reactions occur, being in general the homogeneous catalyst more prone to side products than its heterogenous counterpart, limiting the catalytic potential of homogeneous compounds in Olefin Cyclopropanation [21].

Table 5.1. Cyclopropanation of various olefins using EDA with MCM41-BCu[a]

Olefin	Product	Yield (%)[b] and Selectivity (cis : trans)[c]	
		$[Cu(NCCH_3)_6][B(C_6F_5)_4]_2$	MCM41-BCu
		**79** (32 : 68)	**57** (45 : 55)
		**96** (17 : 83)	**9** (77 : 23)
		**84** (38 : 62)	**65** (37 : 63)
		**37** (0 : 100)	**32** (0 : 100)
		**76** (24 : 76)	**14** (8 : 92)

[a] Catalyst:olefin = 1:250.

[b] Based on EDA conversion.

[c] GC–MS; temperature = 25 °C; reaction time = 24 h.

Some important observations have to be noted: for heterogeneous MCM41-BCu it is quite obvious that the steric hindrance plays a significant role to lower the product yield, when changing the methyl group positions of the examined olefins. However, after grafting, the cationic complex $[Cu(NCCH_3)_6]$ is still accessible due to the anchoring off of the

$B(C_6F_5)_3$ moiety. In general, however, the selectivity of $[Cu(NCCH_3)_6][B(C_6F_5)_4]_2$ is better than that of MCM41-BCu, which is likely due to the steric hindrance inside the pores of the mesoporous material. In terems of yield MCM41-BCu is comparable to Cu(II) immobilized on polymer P4VP [10].

Table 5.2. Cyclopropanation of styrene over various catalysts using EDA[a]

Catalysts	Run	Yield (%)[b]	Selectivity (cis : trans)
MCM41	-	0	-
MCM41-$HNEt_2Ph$	-	< 5	
Leaching test	-	5	(36 : 64)
No catalyst	-	0	-
MCM41-BCu	First run	57	(45 : 55)
	Second run	46	(45 : 55)
	Third run	42	(41 : 59)
	Fourth run	42	(41 : 59)

[a] Catalyst:olefin = 1:250.

[b] Based on EDA conversion; temperature = 25 °C; Reaction time = 24 h.

The catalytic activities of the heterogeneous sample were examined for several runs in the cyclopropanation of styrene as presented in Table 5.2. The activity of such an immobilized catalyst obviously decreases somewhat in the second run, but remains stabile after the third run. With respect to leaching experiments, the filtered solution shows product yields of ca. 5 % formed product after the separation from the immobilized catalyst during the first run. The observed decrease in activity during the first two runs of the recycling experiments seems to be partially due to the adsorption of reactant/product molecules in the channels of the mesoporous materials and, to a minor extent, to the loss of both active and deactivated (inactive) Cu-containing decomposition products. Since this change in activity occurs largely during the first runs catalyst leaching in general is not pronounced. Pure MCM41 shows no activity in the catalytic reaction. In contrast very low catalytic activity also can be found in the case of NEt_2Ph grafted on the surface of mesoporous MCM41.

5.3. Conclusion

Modified Mesoporous MCM41 carrying $B(C_6F_5)_3$ moieties and playing the role of non coordinating heterogeneous anions has been prepared and proved to be a good medium to anchor the cationic $[Cu(NCCH_3)_6]$ complex. The catalyst shows relatively high product yields in olefin cyclopropanation at room temperature and remains active and stabile for several catalytic runs. However, its selectivity is not as good as in case of the homogeneous $[Cu(NCCH_3)_6][B(C_6F_5)_4]_2$.

6. Experimental section

6.1. General procedure

6.1.1. Inert gas atmosphere

All preparations and manipulations were carried out under argon atmosphere using standard Schlenk techniques and all solvents were dried by standard procedures. Unless otherwise stated, all the chemicals were used as received from Aldrich. The glassware were cleaned on a KOH/isopropanol bath followed by HCl bath to remove traces of base and then washed with distilled water. Before use they were heated to dryness in a drying oven to 150 ºC and then cooled under oil pump vacuum.

6.1.2. Solvents

All the organic solvents used were dried, kept under inert gas atmosphere and molecular sieves (4 Å or 3 Å for acetonitrile) prior to use. Diethyl ether, toluene, acetonitrile and n-hexane were dried in a Grubbs apparatus. Methylen chloride was pre dried over P_2O_5 and then distilled over CaH_2. THF was kept over Na and then disilled shortly before use.

6.1.3 Low temperature reactions

The reaction mixtures were cooled down using dry ice/acetone mixtures (~ -78 ºC).

6.2. Characterization methods

Microanalyses were performed at the Mikroanalytisches Labor of the Technische Universität München. Metal analyses were determined with a Vario EL metal analyzer. Atomic absorption spectroscopy (AAS; Varian SpectrAA-400 spectrometer) was used to determine the Metal content. IR spectra were measured with a Unican Mattson Mod 7000 FTIR spectrometer using KBr pellets. EPR spectra were recorded with a JEOL JES-RE2X at X-band frequency ($\nu \approx$

9.05 GHz, microwave power 2mW, modulation frequency 100kHz). Powder XRD data were collected with a Philips X'pert diffractometer using Cu-Kα radiation filtered by Ni. Nitrogen adsorption-desorption measurements were carried out at 77 K, using a gravimetric adsorption apparatus equipped with a CI electronic MK2-M5 microbalance and an Edwards Barocel pressure sensor. Before analysis, calcined MCM-41 was degassed at 723 K overnight to a residual pressure of about 10-24 mbar. A lower degassing temperature of 413 K was used for the modified materials (to minimize destruction of the grafted complex). The specific surface areas (SBET) were determined by the BET method. The total pore volume (VP) was estimated from the N_2 uptake at $p/p_0 = 0.95$, using the liquid nitrogen density of 0.8081 g/cm^3. The pore size distribution curves (PSD, differential volume adsorbed with respect to the differential pore size per unit mass as a function of pore width) were computed from the desorption branch of the experimental isotherms, using a method based on the area of the pore walls. Transmission electron microscopy (TEM) was executed on a JEOL JEM2010 operated at 120 kV. ^{29}Si CP MAS NMR spectra were recorded at 59.627 MHz, with a (7.05 T) Bruker Avance 300 spectrometer, with 5.5 μs ^{1}H 90° pulses, 8 ms contact time, a spinning rate of 5 kHz and 4 s recycle delays. ^{1}H MAS NMR spectra were recorded at 300 MHz using a Bruker Avance 300 spectrometer with 3.0 μs with a spinning rate of 8 kHz. Thermogravimetric analysis (TGA) studies were performed using a Mettler TA 3000 system at a heating rate of 10 K min^{-1} under a static air atmosphere. Mass spectra were measured on a Finnigan MAT 311 and a MAT 90 spectrometer.

6.3. Synthesis and characterization of the compounds described in this work

6.3.1. Homogeneous compounds

$[Cr(NCCH_3)_6][B(C_6F_5)_4]_2$ **(1)**

(0.08 g, 0.64 mmol) $CrCl_2$ was added to a solution of (1.00 g, 1.27 mmol) $Ag[B(C_6F_5)_4]$ in (20 mL) dry acetonitrile. The resulting mixture was stirred overnight in the darkness. The precipitate was removed by filtration and the filtrate was concentrated under vacuum (oil pump) to ca. 3 mL and kept at –35 ºC. The desired product was obtained as a greenish-yellow solid. Yield 0.65 g (61%). Calcd. for $C_{60}H_{18}CrB_2F_{40}N_6$ (1656.38): C 43.50; H 1.09; N 5.07. Found: C 43.41; H 1.04; N 4.74. Selected IR (KBr, cm^{-1}): ν(CN), 2305, 2278.

$[Fe(NCCH_3)_6][B(C_6F_5)_4]_2$ **(2)**

(0.14 g, 0.64 mmol) $FeBr_2$ was added to a solution of (1.00 g, 1.27 mmol) $Ag[B(C_6F_5)_4]$ in (20 mL) dry acetonitrile. The resulting mixture was stirred overnight in the darkness. The precipitate was removed by filtration and the filtrate was concentrated under vacuum (oil pump) to ca. 3 mL and kept at –35 ºC. The desired product was obtained as a brownish orange solid. Yield 0.85 g (80.0%). Calcd. for $C_{60}H_{18}FeB_2F_{40}N_6$ (1660.23): C 43.40; H 1.09; N 5.06. Found: C 43.53; H 1.09; N 4.87. Selected IR (KBr, cm^{-1}): ν(CN), 2314, 2284.

$[Co(NCCH_3)_6][B(C_6F_5)_4]_2$ **(3)**

(0.08 g, 0.64 mmol) $CoCl_2$ was added to a solution of (1.00 g, 1.27 mmol) $Ag[B(C_6F_5)_4]$ in (20 mL) dry acetonitrile. The resulting mixture was stirred overnight in the darkness. The precipitate was removed by filtration and the filtrate was concentrated under vacuum (oil pump) to ca. 3 mL and kept at –35 ºC. The desired product was obtained as a purple solid. Yield 0.81 g (76.4%). Calcd. for $C_{60}H_{18}CoB_2F_{40}N_6$ (1663.32): C 43.33; H 1.09; N 5.05. Found: C 43.01; H 1.08; N 5.33. Selected IR (KBr, cm^{-1}): ν(CN), 2322, 2296.

$[Ni(NCCH_3)_6][B(C_6F_5)_4]_2$ **(4)**

(0.14 g, 0.64 mmol) $NiBr_2$ was added to a solution of (1.00 g, 1.27 mmol) $Ag[B(C_6F_5)_4]$ in (20 mL) dry acetonitrile. The resulting mixture was stirred overnight under exclusion of light. The precipitate was removed by filtration and the filtrate was concentrated under vacuum (oil pump) to ca. 3 mL and kept at –35 ºC. The desired product was obtained as a blue-purple solid. Yield 0.83 g (78.3%). Calcd. for $C_{60}H_{18}NiB_2F_{40}N_6$ (1663.08): C 43.33; H 1.09; N 5.05. Found: C 43.03; H 1.08; N 5.15. Selected IR (KBr, cm^{-1}): ν(CN), 2326, 2300.

$[Cu(NCCH_3)_6][B(C_6F_5)_4]_2$ **(5)**

(0.07 g, 0.64 mmol) $CuCl_2$ was added to a solution of (1.00 g, 1.27 mmol) $Ag[B(C_6F_5)_4]$ in (20 mL) dry acetonitrile. The resulting mixture was stirred overnight in the darkness. The precipitate was removed by filtration and the filtrate was concentrated under vacuum (oil pump) to ca. 3 mL and kept at –35 ºC. The desired product was obtained as a light green solid. Yield 0.66 g (73%). Calcd. for $C_{60}H_{18}CuB_2F_{40}N_6$ (1667.93): C 43.20; H 1.08; N 5.04. Found: C 42.98; H 1.22; N 5.09. Selected IR (KBr, cm^{-1}): ν(CN), 2340, 2317, 2279. EPR: $g_{\|} = 2.405$; $g_{\perp} = 2.085 \pm 0.002$; $A_{\|} = 146 \times 10^{-4} \pm 3\ cm^{-1}$.

$[Cu(NCCH_3)_6][B\{C_6H_3(m\text{-}CF_3)_2\}_4]_2$ **(6)**

(0.069 g, 0.52 mmol) $CuCl_2$ was added to a solution of (1.00 g, 1.04 mmol) $Ag[B\{C_6H_3(m\text{-}CF_3)_2\}_4]$ in 20 mL of dry acetonitrile. . The resulting mixture was stirred overnight in darkness. The precipitate was removed by filtration and the filtrate was concentrated under vacuum (oil pump) to ca. 3 mL and kept at –35 ºC. The desired product was obtained as a sky blue solid. Yield: 0.86 g (81%). Calcd. for $C_{76}H_{42}CuB_2F_{48}N_6$ (2036.33): C 44.83; H 2.08; N 4.13. Found: C 44.63; H 2.13; N 4.01. Selected IR (KBr, cm^{-1}): ν(CN), 2271, 2303, 2332. EPR: $g_{\|} = 2.405$; $g_{\perp} = 2.085 \pm 0.002$; $A_{\|} = 146 \times 10^{-4} \pm 3\ cm^{-1}$.

$[Zn(NCCH_3)_6][B(C_6F_5)_4]_2$ **(7)**

(0.09 g, 0.64 mmol) $ZnCl_2$ was added to a solution of (1.00 g, 1.27 mmol) $Ag[B(C_6F_5)_4]$ in (20 mL) dry acetonitrile. The resulting mixture was stirred overnight under exclusion of light. The precipitate was removed by filtration and the filtrate was concentrated under vacuum (oil pump) to ca. 3 mL and kept at –35 °C. The desired product was obtained as a white creamy solid. Yield 0.69 g (65.5%). Calcd. for $C_{60}H_{18}ZnB_2F_{40}N_6$ (1669.79): C 43.15; H 1.09; N 5.03. Found: C 42.84; H 1.34; N 5.02. Selected IR (KBr, cm^{-1}): ν(CN), 2324, 2297, 2267.

6.3.2. Heterogeneous compounds

MCM-41 : The following materials; fumed silica (SiO_2), hexadecyl-trimethyl ammonium bromide (CTABr), tetramethyl ammonium hydroxide (TMAOH, 25 wt.%) and sodium hydroxide (NaOH) are used without purification for the synthesis of the mesoporous materials. MCM-41 is synthesized having a typical molar gel composition of: 1 SiO_2: 0.2 NaOH: 0.27 TMAOH: 0.27 CTABr: 60 H2O. A typical synthesis procedure is as follows: first TMAOH is dissolved in water and stirred for 5 min. To this solution fumed silica is slowly added (the resulting solution is designated as A). Another solution B is prepared by mixing CTABr and NaOH in distilled water and stirred for about 30 min. Both these solutions, A and B, are mixed together and a gel is formed. The pH of the resulting gel is adjusted to 11.0 with diluted sulphuric acid, and is aged for 16 h. The gel is transferred into a polyethylene bottle and kept in an oven under air for crystallization at 373 K for 3 days. The obtained solid product is washed repeatedly with water, filtered, and dried at 353 K for 12 h.[1, 2] The as-synthesized MCM-41 is refluxed at 80 °C with acidified methanol (volume ratio of 45 ml methanol : 5 ml HCl) to remove the surfactant. The resulting final product is filtered and washed with methanol/water and dried in an oven at 373 K.[3]

SBA-15: SBA-15 silicas were synthesized according to reported procedures [4] using Pluronic 123 triblock copolymers (poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide); Aldrich) $EO_nPO_{70}EO_n$ as templates. In a typical synthesis, 4.0 g of a $EO_{20}PO_{70}EO_{20}$ copolymer was dissolved in 150 g of 1.6 M HCl. To this solution about 8.50 g of TEOS (tetraethyl orthosilicate) was added and the resulting mixture was stirred until TEOS was dissolved. The final molar gel composition of the synthesis mixture was 6.89×10^{-4} P123 triblock copolymers : 0.24 HCl : 0.041 TEOS : 7.88 H_2O. The mixture was placed in an oven for 24 h at 308 K followed by an additional 24 h at 373 K under static condition. Silica products were filtered, dried, and calcined at 823 K.

P4VP: P4VP provided by Aldrich is used without purification for the synthesis of the grafted materials.

6.3.3. Grafting methods

MCM-41 : The mesoporous molecular sieve MCM-41 (2 g) are first preactivated at 473 K under vacuum (10^{-3} mbar) for 4 h to remove physisorbed water. Then, the activated MCM-41 sample was refluxed with 30 ml toluene solution of $PhNEt_2$ adjusting mol ratios N : OH = 0.6 at 120 °C for 24 hours. To this suspension, $B(C_6F_5)_3$ (mol ratios B : OH = 0.60) was added and agitated for 24 more hours, then washed out with toluene three times and dried in vacuum at room temperature. The $B(C_6F_5)_3$ modified MCM-41 then was treated with 30 ml acetonitrile solution of anhydrous copper(II) nitrate to adjust mol ratios Cu : OH = 0.40. The suspension was agitated for 3 days at 313 K under argon, and then the catalyst was washed out with acetonitrile 3 times and dried in vacuum at room temperature. The resulting grafted sample obtained from this experiment is designated as MCM41-BCu and its parent sample were to be characterized by various analytical and spectroscopic techniques as described before.

SBA-15: SBA-15SNH$_2$ was pre-activated at 473 K under vacuum (10^{-3} mbar) for 4 h to remove any physisorbed water. The sample (1 g) was then treated with 0.6 mmol of the designated complex in 30 mL of dry CH_3CN under an argon atmosphere. The mixture was stirred at 313 K for 3 days. The resulting solution was filtered off and the white solid is repeatedly washed with CH_3CN until all physisorbed complexes are removed from the surface. The washed sample was dried under vacuum at RT. Cu Complex grafted on SBA-15SNH$_2$ is designated as SBA-15-SNH$_2$-CuX$_2$. Prior to the grafting the SBA-15 molecular sieve was heated to 523 K under vacuum (10^{-3} mbar) and kept at that temperature for 6 h to remove physisorbed water. The activated mesoporous molecular sieve (SBA-15; 1 g) was treated with (3-aminopropyl)trimethoxysilane (2 mmol) using dry toluene (30 mL) as solvent under an argon atmosphere at 383 K for 24 h. Then excess silane was removed by filtration followed by repeated washing with dichloromethane. The resulting solid was dried under vacuum at room temperature. The parent SBA-15, and grafted samples were systematically characterized by various analytical and spectroscopic techniques as described before.

P4VP: Grafted P4VP samples are synthesized as follows : 1 g of polymer [P4VP, 2 % cross linker] is dried under vaccum at room temperature and then 0.34 g (0.2 mmol) of complex **5** or 0.41 g (0.2 mmol) of complex **6** are introduced in presence of 30 ml acetonitrile as solvent. The resulting mixture is stirred at 323 K for 24 h and then the polymers grafted with Cu-complexes are washed several times with acetonitrile and dried under vaccum. The parent P4VP, and grafted samples were systematically characterized by various analytical and spectroscopic techniques as described before.

6.3.4. X-ray crystallography

X-ray Crystal Determination for $[Co(NCCH_3)_6][B(C_6F_5)_4]_2$: Suitable single crystalsfor the X-ray diffraction study were grown from acetonitrile. A clear, purple fragment was stored under perfluorinated ether, transferred into a Lindemann capillary, fixed and sealed. Preliminary examinations and data collection were carried out on a kappa-CCD device (NONIUS MACH3) with an Oxford Cryosystems cooling device at the window of a rotating anode (NONIUS FR591) with graphite monochromated Mo-$K\alpha$ radiation (λ =0.71073 Å). Data collection was performed at 123 K within the range $1.73° < \theta < 25.42°$. A total of 34151 reflections were integrated, corrected for Lorentz, polarization and absorption effects and those arising from the scaling procedure for latent decay. After merging (R_{int} = 0.033), 5780 [5190: $I_o > 2\sigma(I_o)$] independent reflections remained and all were used to refine 496 parameters. 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 methyl hydrogen atoms were calculated as a part of rigid rotating groups, with $d_{\text{C–H}}$ = 0.98 A^o and $U_{\text{iso(H)}} = 1.5_{U\text{eq(C)}}$. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2-F_c^2)^2$ and converged

with $R1 = 0.0288$ [$I_o > 2\sigma(Io)$], $wR2 = 0.0719$ [all data], GOF =1.035 and shift/error < 0.001. The final difference-Fourier map shows no striking features.[4] CCDC-686893 (**3**) contains the supplementary crystallographic data for this paper.

6.4. Catalytic reactions

6.4.1 Polymerization of isobutene

For higher screening efficiency, the homopolymerization of isobutene is performed in pressure tubes using a dry box. A maximum of 12 tubes is prepared at the same time. Each tube is filled with 20 ml of dried dichloromethane at –40 °C and the catalyst is added ($C_{Catalyst} = 2.5 \cdot 10^{-4}$ mol/L). A magnetic stirring bar is added to each tube. Various amounts of isobutene, which is condensed into a separate tube previously are added. The pressure tubes are sealed and quickly removed from the dry box. The polymerization is performed using a water quench equipped with a magnetic stirrer at the given temperature.

The polymerization is stopped with 5 ml of methanol and 0.2 g of 2,2´-methylene-bis(4-methyl-6-di-*tert*-butyl)phenole are added to prevent oxidation. The solvents are removed in oil pump vacuum and the remaining polymer is dried in fine vacuum at 30 °C until the weight remained constant. The polymeric products were stored under inert gas atmosphere. In order to prove reproducibility, in all experiments one standard polymerization was performed in the first tube, namely 20 mL dichloromethane, $2.5 \cdot 10^{-4}$ mol/L catalyst , 1.5 g isobutene, reaction time 28 h, reaction temperature 30 °C.

6.4.2. Cyclopropanation reaction

EDA (0.114 g, 1.0 mmol) in 2.0 mL of acetonitrile\Dichloromethane was slowly added (addition time 1 h) to a 4.0 mL acetonitrile\Dichloromethane solution of an olefin (5.0 mmol) and catalyst (0.02 mmol; based on Cu content). The reaction mixture was stirred at 298 K for 24 h. The reaction was followed by GC-MS. After the reaction was finished the products were identified by GC-MS. Products were isolated by flash chromatography. Yields were determined based on the amount of EDA used.

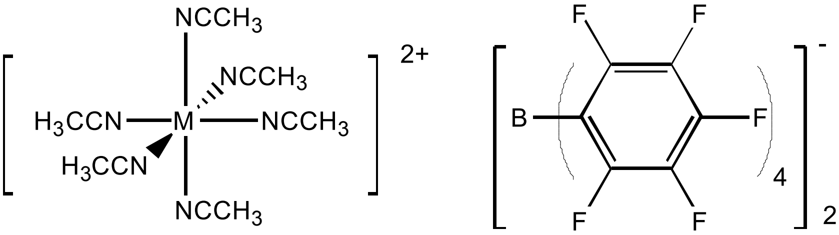
6.4.3. Aldehyde olefination reaction

Different aldehydes (3 mmol), PPh_3 (0.865 g, 3.3 mmol), catalyst (0.01 mmol, based on Cu content, and fluorene (0.2 g, used as internal standard) are dissolved in 15 mL of toluene. The mixture is heated to 353 K and ethyl diazoacetate (EDA; 0.410 g, 3.6 mmol) is - all at once -

added to the solution. After the reaction the catalyst is washed several times with acetone to remove PPh_3, PPh_3O and un-reacted substrate. The reaction is monitored by GC-MS. Yields are determined by GC using a previously recorded calibration curve.

9. Summary

Several complexes of formula $[M^{II}(NCCH_3)_6][B(C_6F_5)_4]_2$ (M = Cr, Fe, Co, Ni, Cu and Zn) have been synthesized and characterized (Chart 9.1). Compounds **(1 - 6)** were prepared by reacting metal (II) halides with silver salts of the anion in acetonitrile (anion exchange). The solvent stabilized complexes were found to be moderately air stable and can therefore be handled in laboratory atmosphere for a brief period of time (minutes). For long term storage (months), the compounds should be kept under an inert gas atmosphere at low temperatures (- 35 °C).



M = Cr **(1)**, Fe **(2)**, Co **(3)**, Ni **(4)**, Cu **(5)**, Zn **(6)**

Chart 9.1.

All compounds are easily accessible and can be obtained in good yields. The FT-IR absorptions indicate that the Zn and Cu complexes have a distorted octahedral structure. Upon thermolysis, solvent is lost from the coordination sphere together with abstraction of fluoride from the anion. However, the different bond strengths of the acetonitrile ligands attached to the same metal centre is not clearly obvious from the TG-MS results. Crystal structure for the cobalt complex **3** has been determined (Figure 9.1) and ideal octahedral coordination for such complexes have been proven.

It was found that the M (II) cations, of formulae **1-6** can be successfully applied as initiators for the polymerization of isobutene at room temperature (scheme 9.1). Highly reactive polyisobutenes with a molecular weight between 800 and 5300 g/mol and with some how high contents of terminal double bonds between 50 and 80% are available by this reaction. The Fe complex is the most-active catalyst, with conversions of up to 88% in 5 hours.

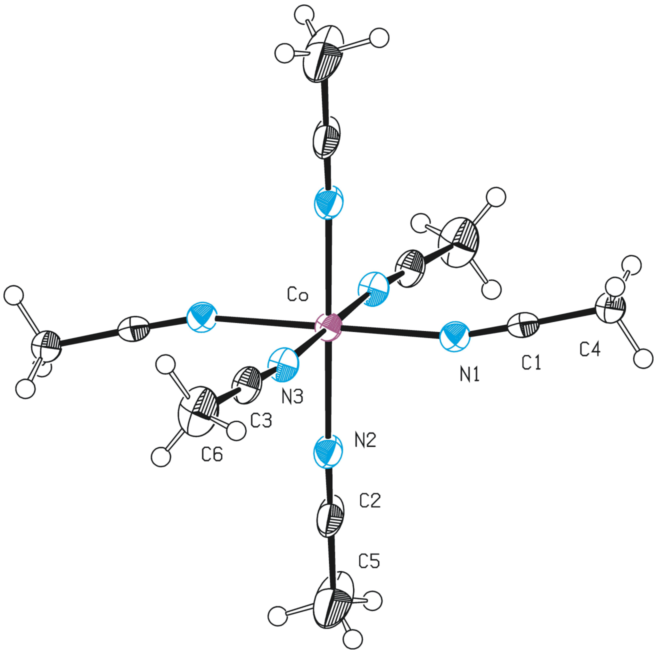
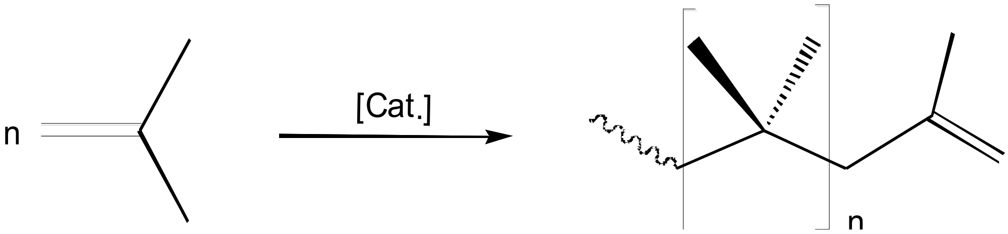


Figure 9.1 ORTEP style plot of the dicationic part of compound **3.**

The average molecular weight (M_n) of the product polymer is 900 $gmol^{-1}$, the polydispersity index (PDI) is 2.33 with 62% terminal double bonds (exo end groups). The Zn complex shows almost the same reactivity, but polymerization proceeds more slowly.

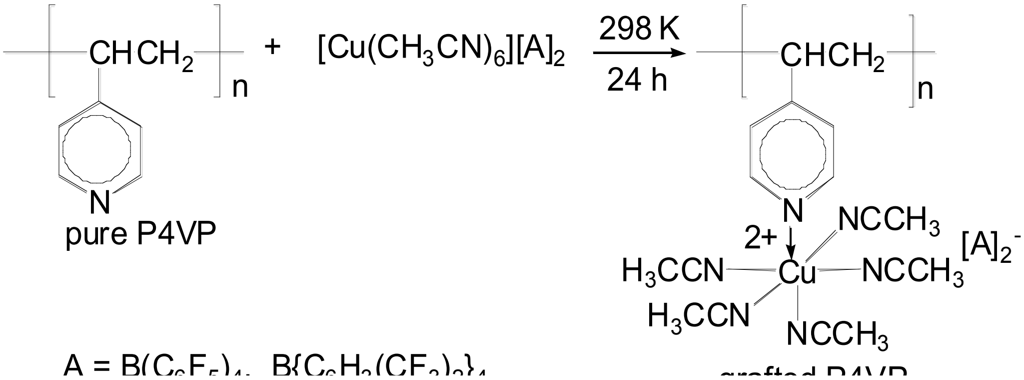


Scheme 9.1. Polymerization of isobutene.

Related to the fact that copper-based complexes have played a prominent role in *in-situ* generation of metal carbenes (or carbenoids) from diazo compounds, two copper complexes, namely $[Cu(NCCH_3)_6][B(C_6F_5)_4]_2$ and $[Cu(NCCH_3)_6][B\{C_6H_3(CF_3)_2\}_4]_2$ have been prepared and heterogenized on mesoporous silica AlMCM-41, SBA-15 and on poly(4-vinylpyridine).

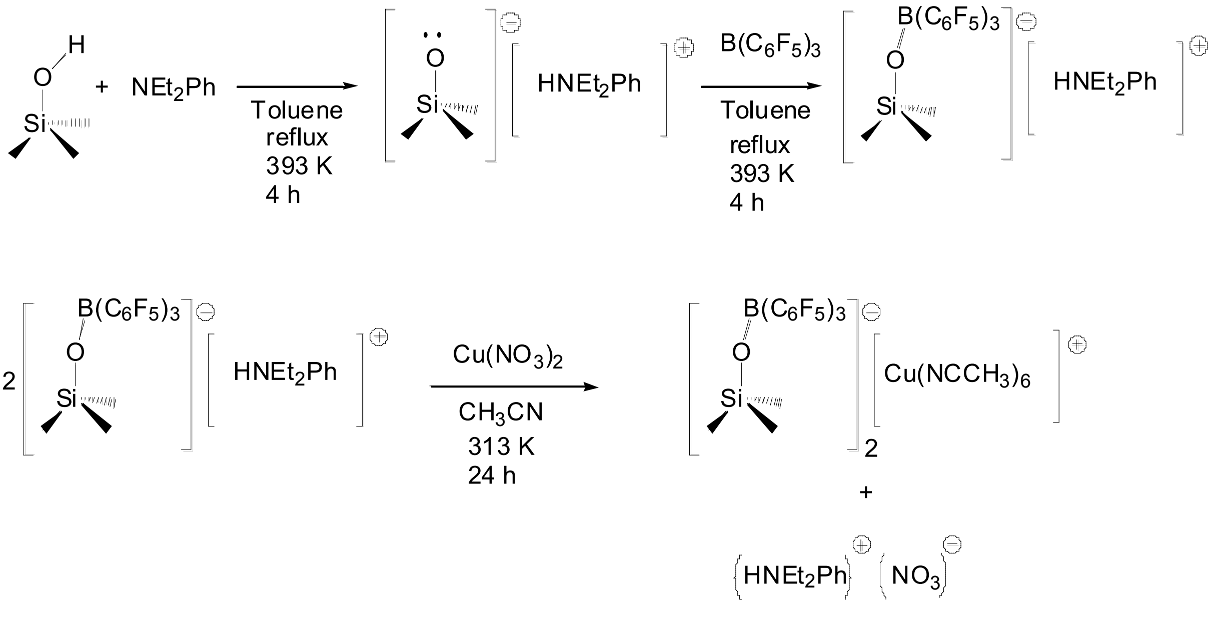
$[Cu(NCCH_3)_6][B\{C_6H_3(CF_3)_2\}_4]_2$ was prepared by reacting Cu (II) chloride with silver salts of the anion in acetonitrile (anion exchange). The complexes $[Cu(NCCH_3)_6][B(C_6F_5)_4]_2$ and

$[Cu(NCCH_3)_6][B\{C_6H_3(CF_3)_2\}_4]_2$ have been successfully grafted on poly(4-vinylpyridine) (scheme 9.2), which was proven by elemental analysis, FTIR and ^{1}H NMR. In the FT-IR spectra of pure P4V one can observe the characteristic stretching vibrations of pyridine rings at ca. 1600 cm^{-1} can be observed. Due to the presence of the coordinated copper (II) ions in the two materials, the vibration mode is shifted to 1605–1620 cm^{-1}, suggesting that there exist donor–acceptor interaction between the pyridine nitrogen atoms and the copper metal. The homogeneous and heterogeneous catalysts are found to be thermally stable and exhibit similar activities in the cyclopropanation of olefins at room temperature. In comparison to the grafted samples, P4VP-supported $[Cu(NCCH_3)_6][B\{C_6H_3(CF_3)_2\}_4]_2$ is more active and leads to better yields in the catalytic reaction. Furthermore, the heterogeneous catalysts are relatively stable in terms of activity for several runs, although the activity decreases after several cycles. The activities of such copper complexes in homogeneous medium are, in general, higher than the activities observed in heterogeneous phase.



Scheme 9.2. Grafting of Cu(II) complexes on the surface of P4VP.

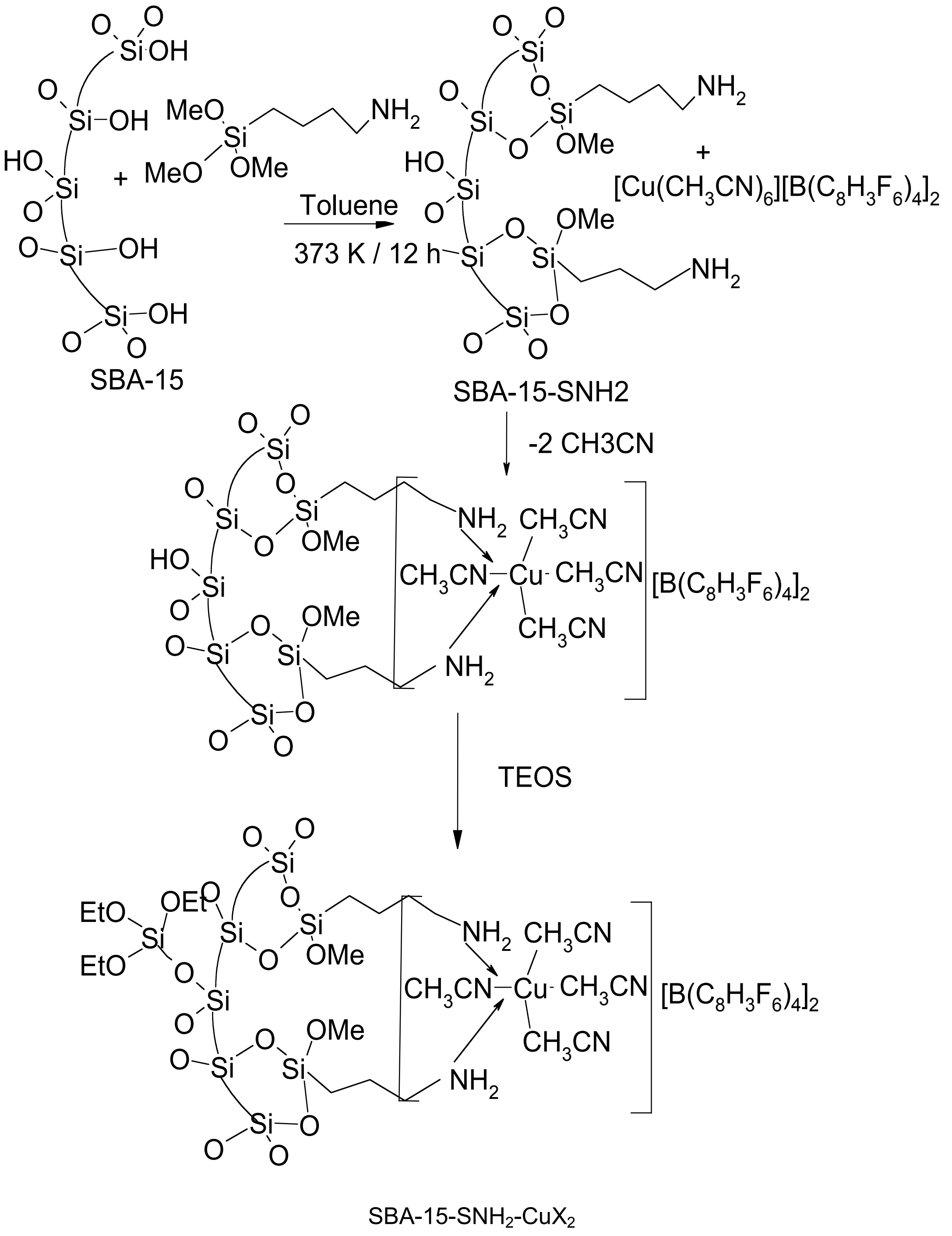
$[Cu(NCCH_3)_6][B(C_6F_5)_4]_2$ is ionically immobilized on AlMCM-41 while the interaction with poly(4-vinylpyridine) is covalent. These techniques of immobilization, however, have some drawbacks, being reflected in some cases in a lower catalytic activity of the immobilized catalysts in comparison to their homogeneous counterparts. A somewhat different approach, namely the immobilization one or two of the counter anions have been also attempted, leaving the cation largely unchanged. Such an anion modified silica surface is obtained by treating the silica surface first with a strong alkylating agent (i.e. BF_3, $B(C_6F_5)_3$, etc.) in the presence of the Brϕnsted base NEt_2Ph. Several modifications are then possible to create the desired cation associated with a surface fixed non coordinating anion (the synthetic steps are depicted in Scheme 9.3.).



Scheme 9.3.

The resulting material was characterized by FTIR, elemental analysis, TEM, GC-MS, TG-MS and powder XRD. Infrared spectra evidence the attachment of $B(C_6F_5)_3$ and the presence of the copper(II) acetonitrile complex on the surface of MCM-41. The TEM measurement for the grafted sample shows that the MCM-41 carrier material retains long range ordering throughout the grafting process and that the channels remain accessible. XRD pattern indicates the grafted sample still to be well ordered. The catalyst was then applied to olefin cyclopropanation at room temperature and similar yields but less selectivity was obtained in comparison to its corresponding homogeneous $[Cu(NCCH_3)_6][B(C_6F_5)_4]_2$.

$[Cu(NCCH_3)_6][B\{C_6H_3(m\text{-}CF_3)_2\}_4]_2$ was heterogenized on the surface of aminosilane modified SBA-15 (scheme 9.4). The resulting material was characterized by FT-IR, TG-MS and elemental analyses, confirming the successful grafting of the copper complex on the surface. The XRD, TEM, and N_2 adsorption isotherms confirm that the surfaces retain long range ordering throughout the grafting process.



Scheme 9.4. Grafting of Cu(II) complex on the surface of SBA-15.

The heterogeneous and homogenous catalysts are found to be of comparable activity for aldehyde olefination reactions. The heterogenized catalyst can be reused for several runs and is applicable in comparatively low amounts.

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Publication originated from this work:

1) Ahmed K. Hijazi, **<u>Akef Al Hmaideen</u>**, Syukri Syukri, Narayanan Radhakrishnan, Eberhardt Herdtweck, Brigitte Voit, and Fritz E. Kühn. *Eur. J. Inorg. Chem* **2008**, 2892–2898

2) Syukri Syukri, Christian E. Fischer, **<u>Akef Al Hmaideen</u>**, Yang Li, Ying Zheng and Fritz E. Kühn. *Microporous. Mesoporous. Mater.* Volume 113, Issues 1-3, 1 August **2008**, Pages 171-177

3) Syukri, Hijazi A. K., Sakthivel A., **<u>Al-Hmaideen A. I.</u>** and Kühn F. E. *Inorganica Chimica Acta* **2007**, 360 (1),197-202.

4) Sakthivel A., Hijazi A. K., **<u>Al Hmaideen A. I.</u>** and Kühn F. E. *Microporous. Mesoporous. Mater.* **2006**, 96, Issues 1-3, 293.

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