Nitrile Ligated Transition Metal Complexes with Weakly Coordinating Counteranions and Their Catalytic Applications

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1. Introduction

Metal cations or complexes stabilized by neutral, nonaqueous ligands are important in numerous synthetic processes,[1–3] and a large variety of such complexes incorporating main group,[4–6] transition metal,[7–12] and lanthanide elements[13–15] surrounded by mono- or bidentate ligands[16] has been prepared during recent decades (see Figure 1).

Among the most promising classes of such compounds for applications both in synthesis and in catalysis are those incorporating easily dissociable solvent ligands (in general donor solvent molecules), with the class of transition metal organonitrile complexes being one of the longest known and best studied.[21]

Since their discovery ca. 150 years ago,[22] many of these nitrile complexes have been synthesized and have found valuable applications. As has been pointed out before, their usefulness results from the labile coordination mode of the ligands, which can be easily replaced by more strongly coordinating ones,[23,24] by other metal cores, or by substrates, thus making the complexes suitable starting materials for the synthesis of other complexes,[20,25] inorganic materials,[26,27] and catalysts.[28]

Using weakly or noncoordinating anions (WCA) as counteranions supports the creation of vacant coordination sites in addition to generating virtually "naked" metal ions.

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The aim of this review is to summarize the organonitrile stabilized transition metal complexes with weakly or noncoordinating anions and their catalytic applications. To achieve this aim, the review is divided into three sections. Section 2, The first of these three sections, provides a brief overview on WCAs applicable in the content of this review. The section 3 summarizes the known transition metal complexes, solely ligated by nitrile molecules and associated with WCAs, their spectroscopic and structural characterization, and their applications. The section 4 describes the possibilities for the anchoring of these compounds to inorganic supports and polymers. Due to the historical development of the research on monomeric and dimeric nitrile ligated complexes, the section 3 is further divided into two subsections. The section 3.1 focuses on the more broadly examined and widely used monomeric complexes, whereas section 3.2 deals with the less common dimeric complexes, which have been known for only about 25 years.[29]

2. Weakly Coordinating Anions as Counterions for Solvent Ligated Transition Metal Complexes

As a result of their ability to enhance the reactivity of metal complexes, the use of weakly or noncoordinating anions as counteranions is of significant interest in both synthesis and catalysis.[30–32] The term "noncoordinating anion" was first created 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 noncoordinating in aqueous solutions.[31] X-ray crystallography proved, however, that in most cases these anions can easily coordinate to cationic centers.[33,34] To account for this observation, the term "weakly coordinating anion" (WCA) was coined, although the strict existence of an anion that has no capability whatsoever for coordination in the condensed phase is nowadays believed to be "as unlikely as that of a free proton".[35,36] It is feasible to obtain conditions where the chemical environment of the ions can be neglected in first approximation.[37,38] Because an anion will preferentially coordinate with the most electrophilic and sterically accessible moiety in its environment, for the generation of more weakly coordinating anions, the anions' negative charge must be delocalized over a large area of nonnucleophilic and chemically robust building blocks.[32] Following this rationale, a multitude of anions have been synthesized during the last decades.[32,39–41] For instance, the exchange of fluorine atoms in BF_4^- ions for phenyl groups leads to the long-known large $[BAr^F_4]^-$ ions ($Ar^F = -C_6F_5$,[42] $-C_6H_3-3,5-(CF_3)_2$,[43] etc.). Examples of other relatively weakly coordinating anions are BPh_4^-, $CB_{11}H_{12}^-$, and related carborane anions, closo borates (*closo*-$[B_{21}H_{18}]^-$,[44] *closo*-

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Fritz E. Kühn studied chemistry at the Technische Universität München (TUM), Germany, where he received his Ph.D. under the direction of W. A. Herrmann in 1994. After a postdoctorate stay in the group of F. A. Cotton (Texas A & M University, USA) 1995−1996, he performed his Habilitation in Munich to become Privatdozent in 2000. From June 2005 to March 2006, he replaced W. A. Herrmann as the Chair of Inorganic Chemistry at TUM. In April 2006, he was appointed Principal Researcher at the Instituto Técnológico e Nuclear (ITN) in Sacavém, Portugal. In December 2006, he returned to TUM as Professor of Molecular Catalysis, and since Oct. 2007 he has additionally been in charge of the Chair of Inorganic Chemistry. F. E. Kühn is author or coauthor of more than 200 scientific papers, is coinventor of a number of patents, and has received several awards for his scientific work.

$[B_{12}F_{12}]^{2-}$,[45] etc.), $[OTeF_5]^-$ 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 $[H(1,8\text{-}C_{10}H_6(BMe_2)_2)]^-$ (hydride sponge).[31]

Several strategies can be applied to introduce a WCA into a system. The abstraction of a methyl-group from $[Cp_2M(CH_3)_x]$ (M = Ti, Zr, Hf, Ta; x = 2, 3) by strong organometallic Lewis acids like $B(C_6F_5)_3$ produces the tight ion pair $[Cp_2MMe^+][MeB(C_6F_5)_3^-]$.[46] Weakly coordinating anions can also be introduced into a system through metathesis reactions of $M^+[A]^-$ ($[A]^-$ = WCA, M = univalent metal, such as Li, Na, K, Ag, Tl) with either labile or covalently bound halide ligands.[40] Furthermore, WCAs can be coordinated via hydride and alkyl abstraction, with the reaction of the $[Ph_3C]^+$ salt of the WCA with $[Cp_2M(CH_3)_x]$ (M = Ti, Zr, Hf, Ta; x = 2, 3) giving $[Cp_2M(CH_3)_{x-1}][A]$ (A = WCA) as a prototype.[32,46] Further information and deeper insights into the field of weakly coordinating anions (e.g., robustness of different WCAs and their influence on chemical reactions) can be gained from the excellent reviews of Krossing and Raabe,[32] Macchioni,[47] and Strauss.[31]

3. Nitrile Ligated Transition Metal Complexes

Complexes of the general formulas $[M(RCN)_{2,4,6}][A]_{1,2}$, $[M(RCN)_6][A]_3$, and $[M_2(RCN)_{8-10}][A]_4$ (M = transition metal ion; A = counterion; R = organic fragment) can be synthesized by several methods, one being the oxidation of metals with nitrosonium salts of the intended counteranion[48] and another the dehydration of aqueous salts.[49] Further synthetic options exist,[50] but the more common method to introduce WCAs to the organonitrile complexes is the above-mentioned usage of metathesis reagents such as silver, potassium, and amine salts (see Scheme 1).[40] All of these reactions have to be carried out in nitrile solvents.

3.1. Monomeric Complexes

Solvent-coordinated monomeric transition metal complexes have been known for a long time.[8,10,48,51−54] Because of their versatile applicability as starting materials for the preparation of other substances or as catalysts, the interest

in these complexes is high and a plethora of new compounds have been synthesized and their uses examined in recent decades.[18,30,55,56]

In the meantime, monomeric complexes bearing weakly coordinating anions of almost every first row transition metal (see Table 1) and some of the second and third row transition metals (see Table 2) have been synthesized and characterized.

3.1.1. Spectroscopic and Structural Characterization

3.1.1.1. Spectroscopic Characterization. All infrared data published so far are summarized in Table 3.

The infrared spectra display CN bands (shifts corresponding to the CN asymmetric stretching vibration) in a range between 2266 and 2354 cm^{-1}, when measured in Nujol mulls or KBr as matrices. Absorbtion in this spectral region is typical for coordinated acetonitrile.

For free acetonitrile, two absorption bands are observed. They can be assigned to the fundamental ν_2-CN stretching mode (2253 cm^{-1}) and the combination mode $\nu_3 + \nu_4$ (2293
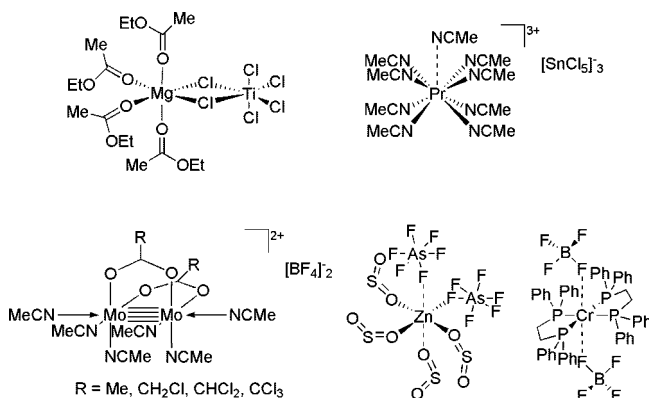
Figure 1. Schematic structures of the complexes MgTiCl$_6$· 4CH$_3$COOC$_2$H$_5$,[1] [Pr(MeCN)$_9$][SnCl$_5$(MeCN)]$_3$,[17] *cis*-[Mo$_2$(*m*-O$_2$-CR)$_2$(MeCN)$_6$][BF$_4$]$_2$ (R = Me, CH$_2$Cl, CHCl$_2$, CCl$_3$),[18] [Zn(SO$_2$)$_4$-(AsF$_6$)$_2$],[19] and [Cr(dppe)$_2$][BF$_4$]$_2$.[20]

Scheme 1. Methods for the Preparation of Organonitrile Complexes with Weakly Coordinating Anions[40,48,49]

$$Cu \ + \ 2\,NOClO_4 \ \xrightarrow[RT]{MeCN} \ [Cu(MeCN)_4][ClO_4]_2 \ + \ 2\,NO$$

$$[M(H_2O)_x][BF_4]_2 \ \xrightarrow[\Delta,\ sieves]{MeCN} \ [M(MeCN)_x][BF_4]_2 \ + \ x\,H_2O \quad (M = Mn,\ Fe,\ Co,\ Ni,\ Cu)$$

$$MnCl_2 \ + \ 2\,Ag[B(C_6H_3(CF_3)_2)_4] \ \xrightarrow[RT]{MeCN} \ [Mn(MeCN)_6][B(C_6H_3(CF_3)_2)_4]_2 \ + \ 2\,AgCl$$
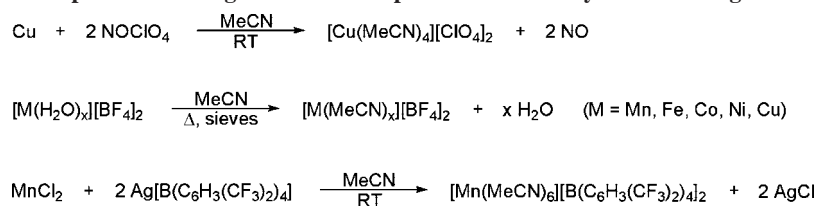
Table 1. Monomeric First Row Transition Metal Complexes

element	cation	anion								
		BF_4^-	ClO_4^-	$CF_3SO_3^-$	PF_6^-	SbF_6^-	AsF_6^-	$B(C_6F_5)_4^{-a}$	$B(C_6H_3\text{-}(CF_3)_2)_4^{-b}$	$(C_6F_5)_3B-C_3H_3N_2-B-(C_6F_5)_3^{-c}$
Ti	$[Ti(MeCN)_6]^{3+}$	+[9]								
V	$[V(MeCN)_6]^{2+}$	+[57]							+[58]	
Cr	$[Cr(MeCN)_6]^{2+}$	+[9]						+[59]	+[58]	
	$[Cr(MeCN)_4]^{2+}$	+[20]								
	$[Cr(PhCN)_4]^{2+}$	+[20]								
	$[Cr(^tBuCN)_4]^{2+}$	+[20]								
	$[Cr(MeCN)_6]^{3+}$	+[60]								
Mn	$[Mn(MeCN)_6]^{2+}$	+[26]	+[61]			+[62]		+[63]	+[58]	+[63]
	$[Mn(MeCN)_4]^{2+}$	+[53]	+[52]	+[49]						
	$[Mn(EtCN)_6]^{2+}$							+[64]		
Fe	$[Fe(MeCN)_6]^{2+}$	+[53]	+[61]	+[49]		+[62,65]		+[59]	+[58]	
	$[Fe(MeCN)_4]^{2+}$	+[57]		+[66]						
Co	$[Co(MeCN)_6]^{2+}$	+[53]	+[52,67]	+[58]		+[62]		+[59]	+[58]	
	$[Co(MeCN)_4]^{2+}$	+[57]			+[68]					
Ni	$[Ni(MeCN)_6]^{2+}$	+[69]	+[70]	+[58]		+[71,72]		+[59]	+[58]	
	$[Ni(PhCN)_6]^{2+}$	+[69]								
	$[Ni(MeCN)_4]^{2+}$	+[57]								
Cu	$[Cu(MeCN)_6]^{2+}$							+[63]	+[63]	+[63]
	$[Cu(MeCN)_4]^{+}$	+[51,57,73]	+[51,74−76]	+[77]	+[50,78−80]			+[81]	+[81]	
	$[Cu(MeCN)_4]^{2+}$	+[53]	+[82]	+[83]						
	$[Cu(MeCN)_2]^{+}$			+[84]				+[81]		
	$[Cu(PhCN)_4]^{+}$	+[77]	+[77,85]		+[77]					
	$[Cu(EtCN)_4]^{+}$		+[21]							
	$[Cu(C_6H_4NO_2CN)_4]^{+}$		+[21]							
	$[Cu(C_7H_7OCN)_4]^{+}$		+[21]							
	$[Cu(C_{10}H_7CN)_4]^{+}$		+[21]							
Zn	$[Zn(MeCN)_6]^{2+}$						+[19]	+[59]		
	$[Zn(PhCN)_6]^{2+}$						+[19]			
	$[Zn(C_6F_5CN)_6]^{2+}$						+[19]			
	$[Zn(MeCN)_4]^{2+}$	+[53]	+[52]							

$^a\ B(C_6F_5)_4^-$ = [structure]; $^b\ B(C_6H_3(CF_3)_2)_4^-$ = [structure]; $^c\ (C_6F_5)_3B-C_3H_3N_2-B(C_6F_5)_3^-$ = [structure]

cm^{-1}).[58] For coordinated acetonitrile, only one band, the fundamental, is expected. This one band can be observed for some of the Pd, Ag, and Pt compounds, as well as for all analyzed Rh, Pt, and Au complexes.

Apart from these few exceptions, the infrared spectra of the complexes exhibit two absorptions. These two bands occur due to Fermi resonance interactions between the ν_2-CN fundamental and the $\nu_3 + \nu_4$ combination bands.

Additional absorptions, as described for $[Cr(MeCN)_6]$-$[B(C_6H_3(CF_3)_2)_4]_2$, $[Zn(MeCN)_6][B(C_6F_5)_4]_2$, and $[Cu$-$(MeCN)_6][A]_2$ (A= $B(C_6F_5)_4^-$, $B(C_6H_3(CF_3)_2)_4^-$, $(C_6F_5)_3B-$ $C_3H_3N_2-B(C_6F_5)_3^-$), are due to different coordination strengths of the acetonitrile ligands and either (a) indicate the inclusion of free acetonitrile in the solid or (b) may originate from (partial) oxidation of the metal center. Accordingly, these vibrations are indicative of the pureness and the coordination geometry of the complexes and deserve particular attention.
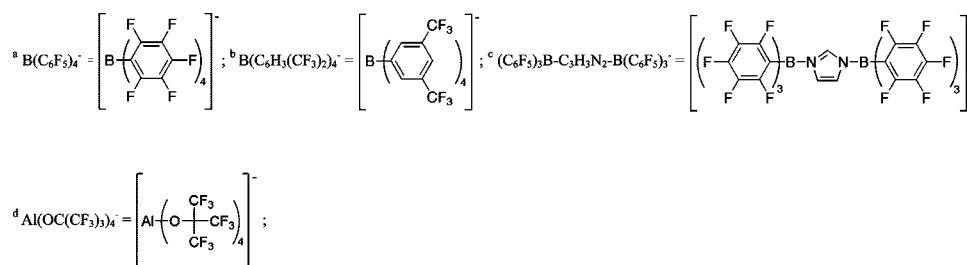
The energies of the detected IR ν_{CN} absorptions for the coordinated nitriles are, with the exception of the combination modes of $[Cu(MeCN)_4][BF_4]$ and $[Ag(MeCN)_4][B(C_6F_5)_4]$, higher than the corresponding bands of free nitrile. Numerous effects have to be considered to explain the positive shift in the CN stretching frequencies. Among these, one of the most important reasons is that this shift is due to the strengthening of the σ bonding between carbon and nitrogen when coordinated to a Lewis-acidic metal center via the nitrogen atom of the nitrile. This results in an increasing force constant, thus an increasing stretching frequency.

Within different series of $[M(NCMe)_{4,6}][A]_2$ (M = V^{2+}, Cr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}), no special trend in the energies of the ν_{CN} can be observed. Since most of the complexes show band splitting due to Fermi resonance, in order to compare the CN stretching frequencies, an average ν_{CN} would be required and, therefore, the integrated intensities of each band are necessary. To generate such useful data additional experimental work has to be performed. The results might lead to a better understanding of the catalytic

Table 2. Monomeric Second and Third Row Transition Metal Complexes.

		anion								
element	cation	BF_4^-	ClO_4^-	$CF_3SO_3^-$	PF_6^-	SbF_6^-	$B(C_6F_5)_4^{-a}$	$B(C_6H_3\text{-}(CF_3)_2)_4^{-b}$	$(C_6F_5)_3B\text{−}C_3\text{-}H_3N_2\text{−}B(C_6F_5)_3^{-c}$	$Al(OC(CF_3)_3)_4^{-d}$
Tc	$[Tc(MeCN)_6]^{2+}$	+[86]								
Ru	$[Ru(PhCN)_6]^{2+}$			+[87]						
Rh	$[Rh(MeCN)_6]^{3+}$	+[88]								
Pd	$[Pd(MeCN)_4]^{2+}$	+[89−91]		+[90]		+[92]				
	$[Pd(EtCN)_4]^{2+}$			+[90]						
Ag	$[Ag(MeCN)_4]^+$	+[93]	+[75]	+[94]	+[95]		+[96]		+[97]	+[98]
	$[Ag(MeCN)_2]^+$							+[97]		
	$[Ag(EtCN)_4]^+$	+[11]					+[64]			
	$[Ag(EtCN)_2]^+$	+[11]								
	$[Ag(C_7H_7CN)_4]^+$	+[11]								
Pt	$[Pt(MeCN)_4]^{2+}$	+[99]		+[90,100]		+[92]				
	$[Pt(EtCN)_4]^{2+}$			+[90]						
Au	$[Au(MeCN)_2]^+$		+[101]	+[102]	+[102]	+[92,103]				

^{a} $B(C_6F_5)_4^-$ = [structure]; ^{b} $B(C_6H_3(CF_3)_2)_4^-$ = [structure]; ^{c} $(C_6F_5)_3B\text{−}C_3H_3N_2\text{−}B(C_6F_5)_3^-$ = [structure]

^{d} $Al(OC(CF_3)_3)_4^-$ = [structure];

activities of the complexes (see below) and help to rationally design optimal catalysts for their particular application fields.

^{1}H NMR data are listed in table 4. Because of different donor qualities of the individual metal centers in comparison to the acetonitrile ligands, the ^{1}H NMR signals of the diamagnetic compounds corresponding to the methyl group of the acetonitrile ligands were observed as being shifted to slightly higher or lower fields in comparison to uncoordinated MeCN (2.10 ppm in $CDCl_3$, 2.00 ppm in CD_3NO_2, 1.95 ppm in CD_3CN, and 1.93 ppm in CD_2Cl_2). For paramagnetic acetonitrile complexes, ^{1}H NMR spectra are different. Because considerable spin density is induced on the ligands and selective spin transferred to the γ protons of acetonitrile, the signals are strongly shifted to high frequencies (162−176 ppm for comparable chromium(III) complexes).[104] In the case of the solid-state ^{1}H NMR of $[Cr(MeCN)_4][BF_4]_2$, the signal appears at 180 ppm;[20] $[Tc(MeCN)_6][BF_4]_2$ displays a signal at 70.3 ppm in CD_3CN.[86]

UV/vis spectra of the complexes showing d → d transitions for the metal centers are summarized in Table 5.

3.1.1.2. Structural Characterization. This section summarizes the structural information available for the monomeric complexes described above. The complexes for which X-ray crystal structures are determined so far are listed in Table 6, with the key bond lengths and angles as well as the appropriate references.

The geometry around the Cr^{2+} and Cu^{2+} ions in $[M(MeCN)_4][A]_2$ is (highly) distorted octahedral with square-planar arranged acetonitrile ligands and fluorine (in the case of BF_4^-) or oxygen atoms (in the case of $CF_3SO_3^-$) of the counterions occupying the apical positions. The cationic part of the complexes $[M(MeCN)_4][SbF_6]_2$ (M = Pd^{2+}, Pt^{2+}) is square-planar as well.

In $[M(RCN)_6][A]_2$ complexes (M(II) = Mn^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Tc^{2+}, Rh^{2+}; A = BF_4^-, $B(C_6F_5)_4^-$, SbF_6^-, AsF_6^-; R = Me, Et, Ph, C_6F_5; M(III) = Cr^{3+}, Rh^{3+}; A = BF_4^-; R

= Me,), the metal center is almost perfectly octahedrally surrounded by six nitrile ligands.

All monovalent copper ions shown in the table that are ligated by four nitrile molecules have slightly distorted tetrahedral coordination environments.

The copper atom in $[Cu(MeCN)_2][B(C_6F_5)_4]$ is linearly coordinated. The X-ray structure of the crystal also reveals weak interactions between the copper ion and the fluorine atoms of the counteranion.

In closely related Ag(I) and Au(I) complexes, similar observations were made.

As can be also observed for comparable Fe, Cu, and Zn complexes, the metal−N bond distances are always in the same range. This fact indicates that these bonds are not strongly influenced by the exact composition of the nitrile ligands or the counterions.

In Figure 2, the diverse coordination environments around metal ions are shown for copper complexes as examples.

Figures 3 and 4 show schematic drawings of the complexes for which the structure has been determined by X-ray spectroscopy.

3.1.2. Applications

Complexes of the type $[M(MeCN)_6][(BF_4)]_2$ (M = Mn, Fe, Co, Ni)[26,105] and $[M(MeCN)_6][(SbF_6)]_2$ (M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+})[62] are good starting materials for the synthesis of molecule-based magnets.

The complexes $[M(MeCN)_n][(BF_4)]_2$ (M = Pd^{II} or first row transition metal ions, n = 4, 6) exhibit high activities for cationic (methyl)cyclopentadiene polymerization in a homogeneous phase (see Scheme 2).[106]

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 7).[57]

Table 3. IR Data of Selected Monomeric Complexes.

compound	ν(CN) [cm^{-1}]	matrix	ref
[V(MeCN)$_6$][B(C$_6$H$_3$(CF$_3$)$_2$)$_4$]$_2$	2291 (m) 2320 (m)	Nujol	40, 58
[Cr(MeCN)$_4$][BF$_4$]$_2$	2305 (m) 2333 (m)	Nujol	49, 58
[Cr(MeCN)$_6$][B(C$_6$F$_5$)$_4$]$_2$	2278 (s) 2305 (s)	KBr	59
[Cr(MeCN)$_6$][B(C$_6$H$_3$(CF$_3$)$_2$)$_4$]$_2$	2277 (w) 2297 (m) 2324 (m)	Nujol	40, 58
[Cr(MeCN)$_6$][BF$_4$]$_3$	2301 2331		60
[Mn(MeCN)$_4$][BF$_4$]$_2$	2283 (m) 2307 (m)	Nujol	58
[Mn(MeCN)$_4$][ClO$_4$]$_2$	2285 (s) 2300 (s)	Nujol	52
[Mn(MeCN)$_4$][CF$_3$SO$_3$]$_2$	2281 (s) 2311 (s)	Nujol	49
[Mn(MeCN)$_6$][B(C$_6$F$_5$)$_4$]$_2$	2284 2312	KBr	64
[Mn(MeCN)$_6$][B(C$_6$H$_3$(CF$_3$)$_2$)$_4$]$_2$	2288 (m) 2315 (m)	Nujol/KBr	40, 58/64
[Mn(MeCN)$_6$][(C$_6$F$_5$)$_3$B−C$_3$H$_3$N$_2$−B(C$_6$F$_5$)$_3$]$_2$	2286 2312	KBr	64
[Fe(MeCN)$_6$][BF$_4$]$_2$	2287 (m) 2310 (m)	Nujol	49, 53, 58
[Fe(MeCN)$_6$][CF$_3$SO$_3$]$_2$	2285 (s) 2314 (s)	Nujol	49
[Fe(MeCN)$_6$][B(C$_6$F$_5$)$_4$]$_2$	2284 (s) 2314 (s)	KBr	59
[Fe(MeCN)$_6$][B(C$_6$H$_3$(CF$_3$)$_2$)$_4$]$_2$	2291 (m) 2318 (m)	Nujol	40, 58, 60
[Co(MeCN)$_6$][BF$_4$]$_2$	2292 (m) 2316 (m)	Nujol	49, 53, 60
[Co(MeCN)$_6$][ClO$_4$]$_2$	2285 (s) 2310 (s)	Nujol	52
[Co(MeCN)$_6$][CF$_3$SO$_3$]$_2$	2293 (s) 2320 (s)	Nujol	49
[Co(MeCN)$_6$][B(C$_6$F$_5$)$_4$]$_2$	2296 (s) 2322 (s)	KBr	59
[Co(MeCN)$_6$][B(C$_6$H$_3$(CF$_3$)$_2$)$_4$]$_2$	2295 (m) 2321 (m)	Nujol	40, 58
[Ni(MeCN)$_6$][BF$_4$]$_2$	2292 (m) 2316 (m)	Nujol	49, 58
[Ni(PhCN)$_6$][BF$_4$]$_2$	2285		69
[Ni(MeCN)$_6$][SbF$_6$]$_2$	2299 2320	AgCl, AgBr	72
[Ni(MeCN)$_6$][CF$_3$SO$_3$]$_2$	2299 (s) 2326 (s)	Nujol	49
[Ni(MeCN)$_6$][B(C$_6$F$_5$)$_4$]$_2$	2300 (s) 2326 (s)	KBr	59
[Ni(MeCN)$_6$][B(C$_6$H$_3$(CF$_3$)$_2$)$_4$]$_2$	2299 (m) 2326 (m)	Nujol	40, 58
[Cu(MeCN)$_2$][B(C$_6$F$_5$)$_4$]	2302 (m) 2332 (m)	Nujol	81
[Cu(MeCN)$_2$][CF$_3$SO$_3$]	2290 (s, m)	Nujol, KBr	84
[Cu(MeCN)$_4$][BF$_4$]	2270 2290	Nujol	51
[Cu(MeCN)$_4$][BF$_4$]$_2$	2300 (m) 2322 (m)	Nujol	49, 53
[Cu(MeCN)$_4$][ClO$_4$]	2275/2270 2300	Nujol/Nujol, C$_4$Cl$_6$	51/21
[Cu(EtCN)$_4$][ClO$_4$]	2282	Nujol, C$_4$Cl$_6$	21
[Cu(PhCN)$_4$][ClO$_4$]	2248	Nujol, C$_4$Cl$_6$	21
[Cu(C$_6$H$_4$NO$_2$CN)$_4$][ClO$_4$]	2247	Nujol, C$_4$Cl$_6$	21
[Cu(C$_7$H$_7$OCN)$_4$][ClO$_4$]	2234	Nujol, C$_4$Cl$_6$	21
[Cu(C$_{10}$H$_7$CN)$_4$][ClO$_4$]	2228	Nujol, C$_4$Cl$_6$	21
[Cu(MeCN)$_4$][ClO$_4$]$_2$	2315 (s) 2325 (s)	Nujol	52
[Cu(MeCN)$_4$][PF$_6$]	2277 (m) 2305 (m)	Nujol	50
[Cu(MeCN)$_4$][B(C$_6$F$_5$)$_4$]	2276 (m)/2277 (vs) 2306 (m)/2308 (s)	Nujol/KBr	81/96, 116
[Cu(MeCN)$_4$][B(C$_6$H$_3$(CF$_3$)$_2$)$_4$]	2286 (s) 2317 (w)	KBr	96, 116

Table 3. Continued.

compound	ν(CN) [cm^{-1}]	matrix	ref
[Cu(MeCN)$_4$][(C$_6$F$_5$)$_3$B−C$_3$H$_3$N$_2$−B(C$_6$F$_5$)$_3$]	2286 (s)	KBr	96, 116
	2318 (w)		
[Cu(MeCN)$_6$][B(C$_6$F$_5$)$_4$]$_2$	2279	KBr	63
	2317		
	2340		
[Cu(MeCN)$_6$][B(C$_6$H$_3$(CF$_3$)$_2$)$_4$]$_2$	2271	KBr	63
	2303		
	2332		
[Cu(MeCN)$_6$][(C$_6$F$_5$)$_3$B−C$_3$H$_3$N$_2$−B(C$_6$F$_5$)$_3$]$_2$	2263	KBr	63
	2284		
	2313		
[Zn(MeCN)$_4$][BF$_4$]$_2$	2295	Nujol	53
	2320		
[Zn(MeCN)$_4$][ClO$_4$]$_2$	2290 (s)	Nujol	52
	2320 (s)		
[Zn(MeCN)$_6$][B(C$_6$F$_5$)$_4$]$_2$	2267 (s)	KBr	59
	2297 (s)		
	2324 (s)		
[Tc(MeCN)$_6$][BF$_4$]$_2$	2280	solid-state	86
	2319		
[Rh(MeCN)$_6$][BF$_4$]$_3$	2317 (s)	Nujol, KBr	88
[Pd(MeCN)$_4$][BF$_4$]$_2$	2315 (vw)	Nujol	56, 89, 118
	2335		
[Pd(MeCN)$_4$][SbF$_6$]$_2$·MeCN	2345	AgBr	92
	2348 (s)		
[Pd(MeCN)$_4$][CF$_3$SO$_3$]$_2$	2351	Nujol	90
[Pd(EtCN)$_4$][CF$_3$SO$_3$]$_2$	2331	Nujol	90
[Ag(MeCN)$_4$][B(C$_6$F$_5$)$_4$]	2266	KBr	97
	2286		
[Ag(MeCN)$_2$][B(C$_6$H$_3$(CF$_3$)$_2$)$_4$]	2296	KBr	97
[Ag(MeCN)$_4$][(C$_6$F$_5$)$_3$B−C$_3$H$_3$N$_2$−B(C$_6$F$_5$)$_3$]	2285	KBr	97
[Ag(MeCN)$_4$][Al(OC(CF$_3$)$_3$)$_4$]	2270	KBr	98
	2304		
[Pt(MeCN)$_4$][SbF$_6$]$_2$·MeCN	2354 (s)	AgBr	92
[Pt(MeCN)$_4$][CF$_3$SO$_3$]$_2$	2353	Nujol	90
[Pt(EtCN)$_4$][CF$_3$SO$_3$]$_2$	2334	Nujol	90
[Au(MeCN)$_2$][SbF$_6$]	2342 (vs)	AgBr	92

Table 4. ^{1}H NMR Data of Selected Diamagnetic Monomeric Complexes

compound	δ [ppm]	solvent	T, °C	ref
[Cr(MeCN)$_6$][B(C$_6$F$_5$)$_4$]$_2$	2.16 (s)	CD$_2$Cl$_2$	25	59
[Fe(MeCN)$_6$][B(C$_6$F$_5$)$_4$]$_2$	2.42 (s)	CD$_2$Cl$_2$	25	59
[Ni(MeCN)$_6$][B(C$_6$F$_5$)$_4$]$_2$	2.14 (s)	CD$_2$Cl$_2$	25	59
[Cu(MeCN)$_4$][B(C$_6$F$_5$)$_4$]	1.87	CDCl$_3$	25	96, 116
[Cu(MeCN)$_4$][B(C$_6$H$_3$(CF$_3$)$_2$)$_4$]	2.02	CDCl$_3$	25	96, 116
[Cu(MeCN)$_4$][(C$_6$F$_5$)$_3$B−C$_3$H$_3$N$_2$−B(C$_6$F$_5$)$_3$]	2.13 (s)	CDCl$_3$	25	96, 116
[Zn(MeCN)$_6$][B(C$_6$F$_5$)$_4$]$_2$	2.13 (s)	CD$_2$Cl$_2$	25	59
[Rh(MeCN)$_6$][BF$_4$]$_3$	2.76 (s)			88
[Pd(MeCN)$_4$][BF$_4$]$_2$	2.65 (s)	CD$_3$NO$_2$		56, 89
[Pd(MeCN)$_4$][CF$_3$SO$_3$]$_2$	2.66 (s)	CD$_3$NO$_2$	8	90
[Pd(EtCN)$_4$][CF$_3$SO$_3$]$_2$	3.00 (q)	CD$_3$NO$_2$	−20	90
	1.35 (t)			
[Ag(MeCN)$_4$][B(C$_6$F$_5$)$_4$]	2.07 (s)	CDCl$_3$	25	97
[Ag(MeCN)$_2$][B(C$_6$H$_3$(CF$_3$)$_2$)$_4$]	2.03 (s)	CDCl$_3$	25	97
[Ag(MeCN)$_4$][(C$_6$F$_5$)$_3$B−C$_3$H$_3$N$_2$−B(C$_6$F$_5$)$_3$]	2.10 (s)	CDCl$_3$	25	97
[Ag(MeCN)$_4$][Al(OC(CF$_3$)$_3$)$_4$]	2.01 (s)	CD$_2$Cl$_2$	25	98
[Pt(MeCN)$_4$][CF$_3$SO$_3$]$_2$	2.83 (s)	CD$_3$NO$_2$		90
[Pt(EtCN)$_4$][CF$_3$SO$_3$]$_2$	3.17 (q)	CD$_3$NO$_2$		90
	1.41 (t)			

The complexes [Cr(RCN)$_4$][BF$_4$]$_2$ (R = ^{t}Bu, Ph) display activities comparable to [Cr(MeCN)$_4$][BF$_4$]$_2$;[18] [Mn(MeCN)$_6$]-[B(C$_6$H$_3$(CF$_3$)$_2$)$_4$]$_2$ with its more weakly coordinating anion shows a significantly higher activity than [Mn(MeCN)$_4$]-[BF$_4$]$_2$.[57] With the exception of [Pd(MeCN)$_4$][BF$_4$]$_2$, which also can polymerize 2-methylpropene, none of these complexes with tetrafluoroborate as the counteranion are active in the polymerization of other monomers.

For octahedrally coordinated transition metals in the formal oxidation state +2 associated with [BF$_4$]$^-$ counteranions and nitrile ligands, the experimentally determined activity (turn-over frequency, TOF) of the monomeric complexes correlates well with the ligand field stabilization energy as a function of the number of d electrons.[57,107] The lower the stabilization energy of a complex, the higher its activity as initiator is. This observation was interpreted as a support of the (cyclopentadiene) polymerization mechanism proceeding via coordination of a substrate molecule to the metal center by replacing the weakly coordinating solvent ligand. In any case, such an interpretation has to be validated for other substrates.

The initiator activity shows also a significant dependence on the reaction temperature. Due to a strong metal−ligand

Table 5. UV/vis Absorption Data of Selected Monomeric Complexes

compound	λ_{max} [nm]	solvent	ref
$[V(MeCN)_6][B(C_6H_3(CF_3)_2)_4]_2$	614	MeCN	40
	444		
$[Cr(MeCN)_4][BF_4]_2$	643	MeCN	49
	616		20
	412		
$[Cr(PhCN)_4][BF_4]_2$	598	CH_2Cl_2	20
	446		
	418		
$[Cr(^tBuCN)_4][BF_4]_2$	644	^tBuCN	20
	432		
	328		
$[Cr(MeCN)_6][B(C_6F_5)_4]_2$	601	MeCN	59
$[Cr(MeCN)_6][B(C_6H_3(CF_3)_2)_4]_2$	1111		40
	645		
$[Mn(MeCN)_4][BF_4]_2$	536	MeCN	49
	408		
$[Mn(MeCN)_6][B(C_6H_3(CF_3)_2)_4]_2$	662	MeCN	40
	524		
	422		
	372		
$[Fe(MeCN)_6][BF_4]_2$	912	MeCN	49
$[Fe(MeCN)_6][CF_3SO_3]_2$	904	MeCN	49
$[Fe(MeCN)_6][B(C_6F_5)_4]_2$	892	MeCN	59
$[Fe(MeCN)_6][B(C_6H_3(CF_3)_2)_4]_2$	917	MeCN	40
$[Co(MeCN)_6][BF_4]_2$	492	MeCN	49
	476		
$[Co(MeCN)_6][CF_3SO_3]_2$	491	MeCN	49
	413		
$[Co(MeCN)_6][B(C_6F_5)_4]_2$	679	MeCN	59
	613		
$[Co(MeCN)_6][B(C_6H_3(CF_3)_2)_4]_2$	1087	MeCN	40
	493		
	472		
$[Ni(MeCN)_6][BF_4]_2$	958	MeCN	49
	582		
	358		
$[Ni(MeCN)_6][CF_3SO_3]_2$	947	MeCN	49
	572		
	499		
$[Ni(MeCN)_6][B(C_6F_5)_4]_2$	679	MeCN	59
	627		
	363		
$[Ni(MeCN)_6][B(C_6H_3(CF_3)_2)_4]_2$	962	MeCN	40
	581		
	564		
$[Cu(MeCN)_6][B(C_6F_5)_4]_2$	774	MeCN	59
$[Zn(MeCN)_6][B(C_6F_5)_4]_2$	853	MeCN	59
	386		

interaction, the activity of the complexes is very low below room temperature. At higher temperatures, for the polymerization of cyclopentadiene, an optimum is reached at about 40 °C and the activity declines, possibly due to decomposition or competitive side reactions, at more elevated temperatures.[57,58]

As mentioned before, the counterions have also a considerable influence on the catalytic performance, since the application of more weakly coordinating anions seems to enhance the activity of the cations decisively. Replacement of the BF_4^- ions by more weakly coordinating anions, for example, $B(C_6F_5)_4^-$, $B(C_6H_3(CF_3)_2)_4^-$, and $(C_6F_5)_3B-C_3H_3N_2-B(C_6F_5)_3^-$, enables the polymerization and copolymerization of other monomers like 2-methylpropene, which are much more difficult to polymerize (see Scheme 3) but of which the resulting polymers are of significantly higher industrial interest.[30]

This is particularly true for the so-called highly reactive polyisobutenes, which contain more than 60% terminal C=C bonds. After functionalization, they are mainly applied as oil additives or lubricants. Each year several 100 000 t of these polymers are industrially produced.[30,108]

The polymerization is currently achieved by means of cationic initiators, such as Lewis acids (e.g., $AlCl_3$, BCl_3, BF_3) in combination with alcohols or water as co-initiators. The problem associated with these processes is not the initiator cost, but the necessary temperature range between −20 and −80 °C, mainly dependent on the molecular weight of the desired products. The need to apply low reaction temperatures stems from the high activity of the initiators that cannot be controlled otherwise.

Another unpleasantry with respect to environmental friendliness of the process is the widespread application of chlorinated solvents. These severe disadvantages of the current industrial process seem to vanish when some of the titled complexes are applied.[30,108]

Complexes $[M(MeCN)_6][A]_2$ (M = Mn^{2+}, Cu^{2+}; A = $B(C_6F_5)_4^-$, $B(C_6H_3(CF_3)_2)_4^-$, $(C_6F_5)_3B-C_3H_3N_2-B(C_6F_5)_3^-$; M = Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}; A = $B(C_6F_5)_4^-$) serve for the polymerization of 2-methylpropene yielding polyisobutylenes at moderate temperatures (between 0 and 60 °C).[30,59,63,64,109] The manganese complexes were also successfully tested for copolymerization of 2-methylpropene and isoprene.

Concerning convenient reaction conditions (e.g., use of nonchlorinated solvents and reaction at room temperature) as well as generation of a high degree of terminal *exo*-double bonds, the best results are reached with $[Cu(MeCN)_6]$-$[B(C_6F_5)_4]_2$ in toluene as the solvent (ca. 90% polymer conversion and 85% terminal *exo*-double bonds at a reaction temperature of 30 °C).[63]

Moreover, copper complexes of the formula $[Cu(MeCN)_4][A]$ (A = BF_4^-, PF_6^-, ClO_4^-, $B(C_6F_5)_4^-$, $B(C_6H_3(CF_3)_2)_4^-$, $(C_6F_5)_3B-C_3H_3N_2-B(C_6F_5)_3^-$) are good starting materials for the synthesis of fluorescent chemosensors[75] and peroxo-bridged dicopper adducts,[74] as well as precursors of catalysts for the (asymmetric) cyclopropanation,[96,110,111] 1,4-addition of diethylzinc to α,β-unsaturated enones,[112] aza-Diels−Alder reactions of *N*-sulfonyl imines,[113] carbenoid insertion of aryl diazoesters into the Si−H bond of silanes,[80] [2 + 2] cycloaddition of 1-methoxyallenylsilane with α-imino esters,[114] and alkene aziridinations (see Table 8).[96,115]

With the complexes $[Cr(RCN)_4][(BF_4)]_2$ (R = Me, ^tBu, Ph) as starting materials, several other chromium(II) derivatives can be synthesized.[20]

$[Mn(MeCN)_6][B(C_6H_3(CF_3)_2)_4]_2$ can be used for the synthesis of paramagnetic solids.[117]

Air oxidation of alkanes can be catalyzed by $[Co(MeCN)_4][(PF_6)]_2$ (see Scheme 4).[68]

The complexes $[Co(MeCN)_6][(BF_4)]_2$ and $[Ni(MeCN)_6]$-$[(BF_4)]_2$ catalyze polymerizations (see Scheme 5) of olefins.[118]

$[Pd(MeCN)_4][(BF_4)]_2$ catalyzes the isomerization,[56,118] dimerizations,[119] and oligomerizations[55] of olefins as well as polymerizations of olefins and acetylenes (see Table 9).[55,118,120,121]

$[Ag(MeCN)_4][A]$ (A = BF_4^-, ClO_4^-) can be used as starting material for the synthesis of cubic clusters,[122] luminescent heterometallic materials,[95,123] coordination polymers,[124] and the synthesis of other transition metal complexes.[108] The complexes $[Ag(MeCN)_4][A]$ (A = $B(C_6F_5)_4^-$, $(C_6F_5)_3B-C_3H_3N_2-B(C_6F_5)_3^-$) 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 6).[97]

Table 6. Selected Bond Lengths and Bond Angles of Monomeric Complexes (M = Metal).

complex	distance [Å]		angle [deg]		ref
	M−N	M−F/M−O	N−M−N	F−M−F	
[Cr(MeCN)$_4$][BF$_4$]$_2$	2.069(2)	2.407(2)	88.85(7)		20
	2.063(2)		91.15(7)		
			180		
[Cr(MeCN)$_6$][BF$_4$]$_3$	1.998(16)				60
	1.996(12)				
	1.999(16)				
	2.004(11)				
[Mn(EtCN)$_6$][B(C$_6$F$_5$)$_4$]$_2$·EtCN	2.247(4)		86.2(12)		64
	2.213(4)		91.0(11)		
	2.214(4)		180		
			93.8(12)		
			89.0(11)		
			87.5(12)		
			180		
			92.5(12)		
			180		
[Fe(MeCN)$_6$][SbF$_6$]$_2$	2.153(2)		88.05(10)		65
[Fe(MeCN)$_4$][CF$_3$SO$_3$]$_2$	2.162(2)	2.091(1)	93.3(7)		66
	2.170(2)		86.8(7)		
[Co(MeCN)$_6$][B(C$_6$F$_5$)$_4$]$_2$	2.098(2)		91.76(6)		59
	2.105(2)		91.63(5)		
	2.137(1)		90.28(6)		
[Ni(MeCN)$_6$][SbF$_6$]$_2$	2.075(3)		91.5(1)		71
			88.5(1)		
[Cu(MeCN)$_2$][B(C$_6$F$_5$)$_4$]	1.844(2)	2.716	180.0(2)	180.0	81
[Cu(MeCN)$_4$][BF$_4$]	1.970^a		105.9^a		73
	1.986^a		107.3^a		
	1.996^a		108.4^a		
	2.022^a		110.5^a		
			111.8^a		
			112.7^a		
[Cu(MeCN)$_4$][ClO$_4$]	1.95^a		106−113		76
	2.01^a				
	2.01^a				
	2.02^a				
[Cu(PhCN)$_4$][ClO$_4$]·PhCN	1.972(3)		116.8(1)		77
	1.975(3)		114.7(1)		
	1.994(3)		108.2(1)		
	2.010(3)		108.0(1)		
			105.8(1)		
			103.6(1)		
[Cu(MeCN)$_4$][CF$_3$SO$_3$]	1.983^a		113.9^a		77
	1.996^a		110.5^a		
	2.007^a		107.8^a		
	2.014^a		109.3^a		
			107.9^a		
			107.0^a		
[Cu(MeCN)$_4$][PF$_6$]·MeCN	1.974^a		113.3^a		79,80
	1.998^a		113.0^a		
	2.010^a		112.2^a		
	2.022^a		107.5^a		
			105.5^a		
			104.7^a		
[Cu(PhCN)$_4$][PF$_6$]	1.970(9)		117.9(3)		77
	1.998(7)		106.5(1)		
	1.998(7)		104.6(3)		
	2.018(9)		108.3(3)		
			102.1(1)		
			118.0(3)		
[Cu(MeCN)$_4$][CF$_3$SO$_3$]$_2$	1.984	2.362			83
	1.987	2.418			
	1.990				
	1.993				
[Cu(MeCN)$_4$][B(C$_6$F$_5$)$_4$]	2.000(2)		104.28(7)		96
	2.021(2)		103.89(7)		
	2.001(2)		103.13(7)		
	2.029(2)		106.26(7)		
			119.81(7)		
			120.57(7)		
[Cu(MeCN)$_6$][B(C$_6$F$_5$)$_4$]$_2$	1.999(2)		89.17(7)		63
	1.987(2)		88.45(6)		
	2.386(2)		90.83(7)		
			91.55(6)		

^{a} Average.

Table 6. Continued.

| | distance [Å] | | angle [deg] | | |
complex	M−N	M−F/M−O	N−M−N	F−M−F	ref
[Zn(MeCN)$_6$][AsF$_6$]$_2$	2.134(2)				19
[Zn(PhCN)$_6$][AsF$_6$]$_2$	2.108(2)				19
	2.140(2)				
	2.126(2)				
	2.149(2)				
	2.135(2)				
	2.157(2)				
[Zn(C$_6$F$_5$CN)$_6$][AsF$_6$]$_2$	2.120(18)				19
	2.151(2)				
	2.128(18)				
[Tc(MeCN)$_6$][BF$_4$]$_2$	2.062(4)		88.8−91.2		86
[Rh(MeCN)$_6$][BF$_4$]$_3$	1.987(3)		91.9(1)		88
	1.984(4)		177.9(1)		
	1.985(3)				
	1.990(4)				
[Pd(MeCN)$_4$][SbF$_6$]$_2$·MeCN	1.98(1)		178.5(5)		90
[Ag(MeCN)$_2$][B(C$_6$H$_3$(CF$_3$)$_2$)$_4$]	2.097(2)		180		97
	2.066(4)		180		
[Ag(MeCN)$_4$][BF$_4$]	2.229(3)−2.316		104.2(1)−115.8(1)		93
[Ag(MeCN)$_4$][CF$_3$SO$_3$]	2.26(1)				94
[Ag(EtCN)$_4$][B(C$_6$F$_5$)$_4$]	2.281(3)		103.4(12)		64
	2.265(3)		125.5(12)		
	2.279(3)		98.8(12)		
	2.298(3)		107.3(12)		
			124.9(12)		
			99.0(12)		
[Pt(MeCN)$_4$][SbF$_6$]$_2$·MeCN	1.97(2)		179(1)		92
[Au(MeCN)$_2$][SbF$_6$]	1.97(1)		180(1)		92,103

[Pt(MeCN)$_4$][(BF$_4$)]$_2$ catalyzes the dimerization of branched olefinic monomers, such as 2-methylpropene, Z-methylbut-2-ene, 2-ethylbut-1-ene, and *cis*- and *trans*-4-methylpent-2-ene (see Scheme 7).[99]

3.2. Dimeric Nitrile Ligated Transition Metal Complexes

As outlined in the previous chapter, mononuclear complexes stabilized solely by solvent ligands are common, but until 1988, the only dinuclear analogues known in the literature were the aqueous cations Rh$_2$(aq)$^{4+}$ and Mo$_2$(aq)$^{4+}$.[88,125] Since then, several dinuclear complexes, soluble in organic solvents, with M$_2^{4+}$ cores that are surrounded exclusively by acetonitrile ligands have been prepared. Compounds having weakly coordinating counteranions have been published for M = Rh,[125,126] Mo,[127] Re,[128] and Tc[129] (see Table 10 and Figure 5).

The structures shown in Figure 5 have been determined by X-ray diffraction or, in the case of [Tc$_2$(MeCN)$_{10}$][BF$_4$],[129] derived from the X-ray structure of closely related complexes.

[Mo$_2$(MeCN)$_{8,10}$]$^{4+}$ displays a quadruple bond,[29,130] [Re$_2$(MeCN)$_{10}$]$^{4+}$[128] and [Tc$_2$(MeCN)$_{8,10}$]$^{4+}$[129] display a triple bond, and [Rh$_2$(MeCN)$_{10}$]$^{4+}$[88,125] displays a single bond.

3.2.1. Spectroscopic and Structural Characterization

Published IR data of dimeric complexes are shown in Table 11. The infrared spectra of [M$_2$(MeCN)$_{8,10}$][A]$_4$ exhibit two or three characteristic ν(CN) stretching vibrations in the range of 2276 and 2359 cm^{-1} corresponding to coordinated acetonitrile ligands. Only for [Mo$_2$(MeCN)$_{10}$][BF$_4$]$_4$ with Nujol as the matrix is a band at 2247 cm^{-1} mentioned in the literature. This value is, surprisingly, lower than that of uncoordinated acetonitrile (2253 cm^{-1}).

Typical ^{1}H NMR values for free acetonitrile are 1.95 ppm in CD$_3$CN, 2.00 ppm in CD$_3$NO$_2$, and 2.05 ppm in C$_3$D$_6$O

and those for free propionitrile are 2.35 and 1.19 ppm. The complexes with acetonitrile as ligand show two peaks, corresponding to the equatorial and axial nitrile or one peak for pure, free acetonitrile (Table 12). That especially axial ligands undergo immediate and fast exchange with coordinating deuterated solvents (especially acetonitrile) supports the assumption of them being particularly weakly coordinated. A similar observation (two peaks in the case of coordinated and four in the case of coexistent coordinated and uncoordinated acetonitrile molecules) can be made with propionitrile as ligand.[88]

The dimeric complexes, which have been structurally characterized by X-ray crystallography, are listed in table 13. In contrast to the dimolybdenum cation with its slightly bent ligands, the dirhodium cations are in an octahedral environment.[130] The center of the Rh−Rh bond resides on a C_2 axis and the equatorial planes of the ligands are twisted with respect to each other, forming an almost perfectly staggered geometry.

Since the Rh−Rh and Rh−N bond distances of all examined complexes (with different nitrile ligands and different counterions) are equal within the error margins, it can be assumed that metal−metal as well as metal−nitrogen bonds are not highly influenced by the identity of ligands or counterions.[88,125]

The equatorial acetonitrile ligands of [Re$_2$(MeCN)$_{10}$]$^{4+}$ are also staggered, and the equatorial ligands are slightly bent as is observed for the dimolybdenum complex.

As mentioned above, in all cases, the equatorial ligands are bound more strongly (i.e., they display shorter metal−nitrogen distances) compared with the axial ligands.[132]

PLATON representations of the cationic parts of exemplary dimeric complexes can be seen in Figure 6.
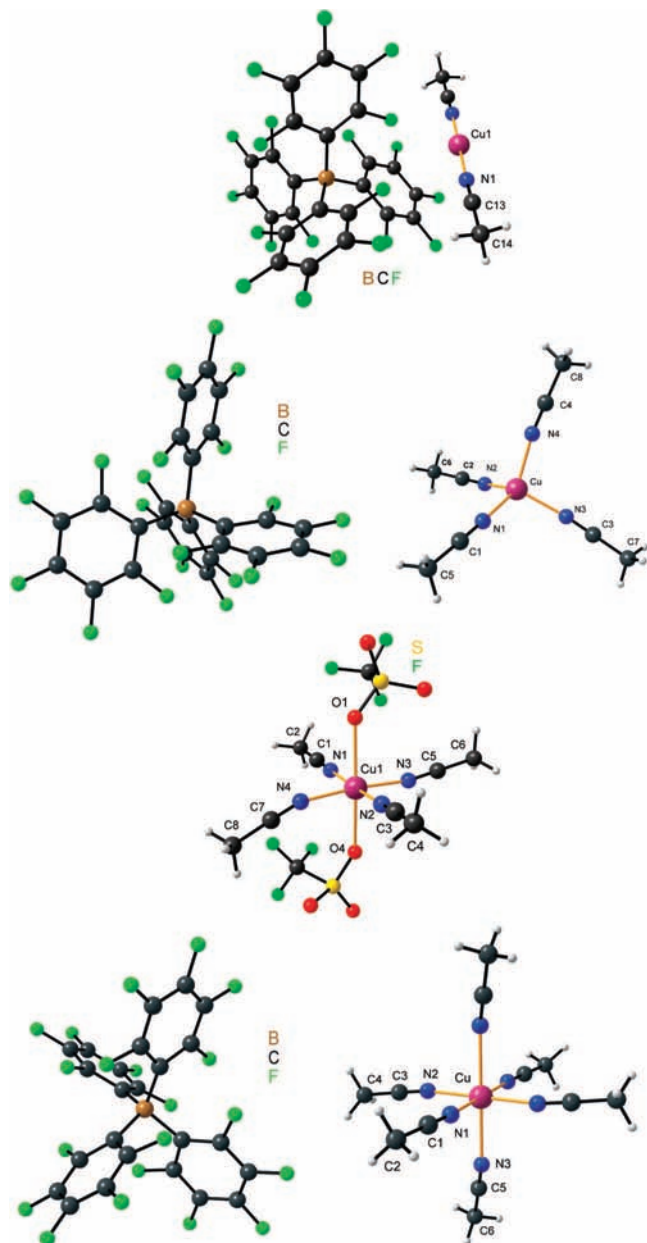
Figure 2. Perspective drawings based on the X-ray crystal structures of the linear $[Cu^I(MeCN)_2][B(C_6F_5)_4]$, the tetrahedral $[Cu^I(MeCN)_4][B(C_6F_5)_4]$, the square-planar $[Cu^{II}(MeCN)_4]$-$[SO_3CF_3]_2$, and one of the noncoordinating anions and the dicationic part of the octahedral $[Cu^{II}(MeCN)_6][B(C_6F_5)_4]_2$.[63,81,83,96]

3.2.2. Applications

In 1993, a study was published with the complexes $[M_2(MeCN)_{10}][BF_4]_4$ (M = Mo^{2+}, Re^{2+}, Rh^{2+}) serving as starting materials for the synthesis of polyoxometallate salts.[133] Three years later, a solvated molecular wire, a new type of mixed-valence, one-dimensional metal chain, $[Rh(MeCN)_4(BF_4)_{1.5}]_\infty$ (see Table 14),[27] was prepared by an electrochemical reduction of $[Rh_2(MeCN)_{10}][BF_4]_4$, but $[Mo_2(MeCN)_8][BF_4]_4$ is the only of the quoted dinuclear complexes for which catalytic applications have been reported in the literature. Besides the possibility of serving as a building block for other dimolybdenum compounds, it shows activity in catalytic alkyne polymerization (see Scheme 8), in cationic cyclopentadiene polymerization, and, with $EtAlCl_2$ as cocatalyst, in the metathesis polymerization of norbornene.[3,134-137]
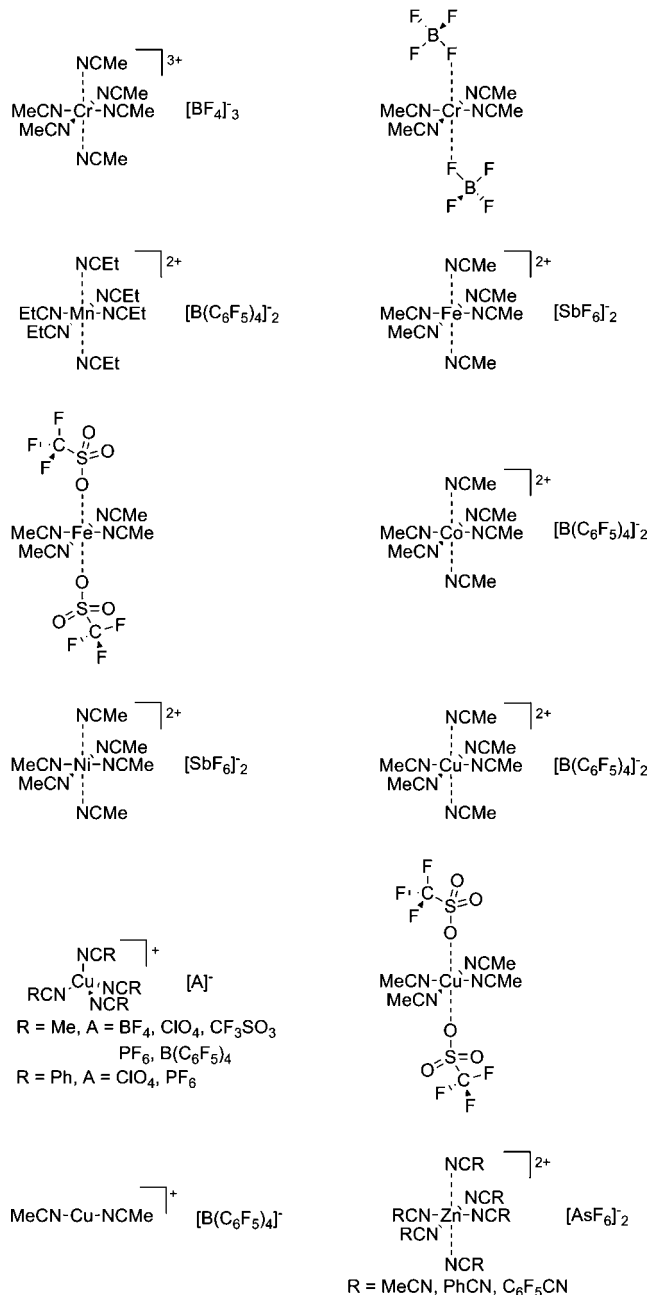
Figure 3. Monomeric first row transition metal complexes with known structures.[19,20,60,63-66,71,76-81,83,86,88,92-94,96,97]

It is interesting to note in the context of metal-containing wires and networks that a reaction of $[Zn(SO_2)_2][AsF_6]_2$ with CF_3CN yields a two-dimensional polymeric network $[Zn(CF_3CN)_2(AsF_6)_2]$ that contains bridging AsF_6^- anions (Zn−F distances, 2.067(6) and 2.090(6) Å) and only two nitriles per zinc in *trans* position with respect to each other, with a Zn−N distance of 2.014(8) Å.[19]

4. Immobilization of the Metal Complexes

The main advantage of homogeneous transition metal catalysts is the possibility of controlling speed and selectivity of a reaction under comparatively mild operating conditions. The problem is that these catalysts are difficult to separate from the products, making their reuse difficult. Because of that, heterogeneous catalysts are in general regarded as being more desirable for use in industrial processes. However, many heterogeneous catalysts often have severe drawbacks,
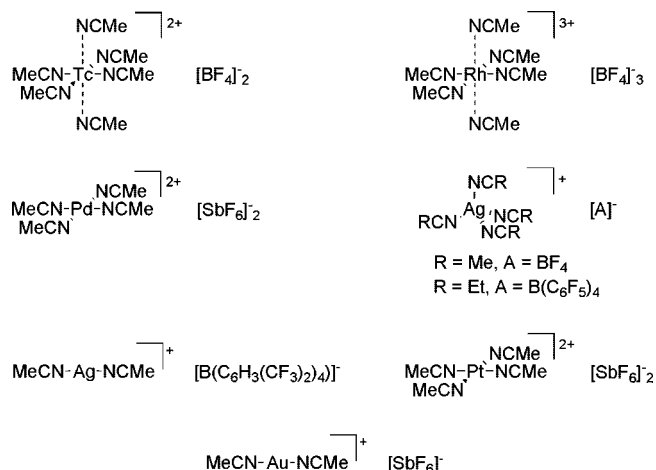
Figure 4. Monomeric second and third row transition metal complexes with known structures.[64,86,88,92,93,97]

Scheme 2. Polymerization of Cyclopentadiene, Yielding the Two Co-existing Polymers
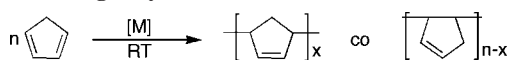
Table 7. Cyclopentadiene Polymerization[a][57]

complex	c_i^b (mol%)	PY^c (%)
$[Mn(MeCN)_6][B(C_6H_3(CF_3)_2)_4]_2$	2.52×10^{-4}	100
$[Mn(MeCN)_4][BF_4]_2$	2.50×10^{-3}	100
$[Zn(MeCN)_4][BF_4]_2$	5.00×10^{-3}	100
$[Fe(MeCN)_4][BF_4]_2$	5.00×10^{-3}	94
$[Cr(MeCN)_4][BF_4]_2$	5.00×10^{-3}	92
$[Ni(MeCN)_4][BF_4]_2$	5.00×10^{-3}	15
$[V(MeCN)_6][BF_4]_2$	5.00×10^{-3}	0

[a] Reaction time = 16 h; temperature = 25 °C; solvent = methylene chloride; c_0(cyclopentadiene) = 9.08 mol %. [b] c_i = concentration of the initiator. [c] PY = polymer yield.

Scheme 3. Polymerization of 2-Methylpropene ("Isobutene" or "Isobutylene")
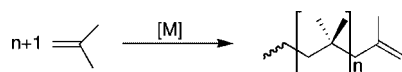
such as low selectivity, low activity, or harsh (energy-intensive) reaction conditions. These drawbacks need to be overcome. One method of combining the advantages of both homogeneous and heterogeneous catalysis is to immobilize homogeneous catalysts. This can be realized by attaching homogeneous catalysts either to organic polymers[138] or to inorganic supports[139] in a manner that the ligand sphere is preserved around the metal and the complex remains accessible.

4.1. Anchoring to Inorganic Supports

For the anchoring of transition metal complexes to inorganic (silica or alumina) supports, several possibilities seem to be feasible.[140] Direct grafting by substitution of a metal-bonded nitrile group by a surface-bound hydroxyl group leads to a reduction of the Lewis acidity of the metal by the formation of an $-O-M$ bond and the loss of HA, where A is one of the counterions of the former transition metal cation.[141] The disadvantage of the reduction of the metal charge is that there is usually an associated pronounced activity loss.[135] Another possibility to heterogenize cations is the exchange of one or two nitrile ligands by a neutral, surface-fixed bidentate Lewis basic donor ligand, which also

leads to the reduction of catalytic activity of the cation by the donation of additional electron density.[106] A third procedure that avoids the drawbacks of the above-mentioned methods is grafting by ionic interactions, that is, the partial ion exchange of H^+ or Na^+ cations present in the surface of mesoporous materials by the transition metal cations.[142]

A different approach is the immobilization of one or several of the counteranions on a silica surface, leaving the cations unbound to the surface, except by ionic interactions with the anions.[143]

In compensation for the (often) reduced catalytic activity, heterogeneous catalysts usually can be reused many times, for example, to polymerize several batches of monomer. Thus, there is now considerable interest in developing new catalysts and finding feasible support materials.

In the 1990s, McCann et al.[3,134,135] 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 regarding the exact nature of the molybdenum species on the surface, that is, whether the Mo−Mo bond is retained (as reported for $[Mo_2(\mu\text{-}O_2CMe)_4]-SiO_2^{139}$) or broken to yield mononuclear species (as observed for $[Mo_2(C_3H_5)_4]-SiO_2^{144}$) (see Figure 7).

Nevertheless, these complexes were tested as initiators for ring-opening metathesis polymerization (ROMP) of norbornene, the polymerization of cyclopentadiene and dicyclopentadiene, and the polymerization of phenylacetylene (for more information, for example, the appropriate schemes, see sections 3.1.2 and 3.2.2, because the mechanisms of the here mentioned reactions are assumed to be the same with the unsupported monomeric and dimeric complexes). The main effect of supporting the dimolybdenum salts on silica was, unfortunately, found to be a severe decrease of their catalytic activity, achieving, for example, a polymer yield of 76% with unsupported and 22% with SiO_2-supported $[Mo_2(MeCN)_8][BF_4]_4$ as initiator for the polymerization of cyclopentadiene (reaction time = 16 h, temperature = 20 °C, solvent = methylene chloride).[3,135]

An exception is the polymerization of norbornene in chlorobenzene. While $[Mo_2(MeCN)_8][BF_4]_4-SiO_2$ polymerizes norbornene at 90 °C with a reaction time of 48 h almost quantitatively (97%), the unsupported $[Mo_2(MeCN)_8][BF_4]_4$ shows, in the absence of $AlEtCl_2$ as cocatalyst, no reaction at any temperature.[134]

In 2000, a study of the heterogenization of the complexes $[Mo_2(\mu\text{-}O_2CMe)_2(MeCN)_6][BF_4]_2$ and $[Mo_2(MeCN)_{10}][BF_4]_4$ on the surface of purely siliceous MCM-41 was presented.[144] MCM (mobile crystalline material), a silicate obtained by a template procedure, is ordered to a certain degree and has variable pore sizes.[145]

MCM-41 consists of a hexagonal packing of one-dimensional channels embedded in a matrix of amorphous silica. The pore diameters are tunable in a range between 20 and 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.[146,147] The structure of MCM-48 consists of two independent and intricately interwoven networks of mesoporous channels. It has a surface area exceeding 1500 m^2 g^{-1}, pore volumes >1 cm^3 g^{-1} and additionally a very narrow pore size distribution.[148,149] Because of the channel network making the pore system

Table 8. Applications for Copper Complexes

a) Styrene cyclopropanation catalysed by [Cu(MeCN)$_4$][A] (A = B(C$_6$F$_5$)$_4$$^-$, B(C$_6H_3$(CF$_3$)$_2$)$_4$$^-$, (C$_6F_5$)$_3$B-C$_3H_3N_2$-B(C$_6F_5$)$_3$)$^-$ using ethyl diazoacetate.[96]

b) Enantioselective 1,4-addition reaction of 2-cyclohexene-1-one with ZnEt$_2$ catalysed by [Cu(MeCN)$_4$][ClO$_4$] and a chiral ligand.[112]

c) Enantioselective Aza Diels-Alder reaction of Danishefsky's Diene with a N-sulfonyl imine catalysed by [Cu(MeCN)$_4$][A] (A = ClO$_4$$^-$, PF$_6$$^-$) in the presence of a chiral ligand and TFA.[113]

d) Asymmetric carbenoid insertion into the Si-H bond of triphenylsilane mediated by [Cu(MeCN)$_4$][PF$_6$] and a chiral ligand.[80]

e) Enantioselective [2+2] cycloaddition reaction of 1-methoxyallenylsilane with an α-imino ester by means of [Cu(MeCN)$_4$][A] (A = ClO$_4$$^-$, PF$_6$$^-$, BF$_4$$^-$) and a chiral ligand.[114]

f) Aziridination of an olefin catalysed by [Cu(MeCN)$_4$][A] (A = B(C$_6$F$_5$)$_4$$^-$, B(C$_6H_3$(CF$_3$)$_2$)$_4$$^-$, (C$_6F_5$)$_3$B-C$_3H_3N_2$-B(C$_6F_5$)$_3$)$^-$) using PhI=NTs.[96,116]

Scheme 4. Oxidation of Cyclohexane[68]
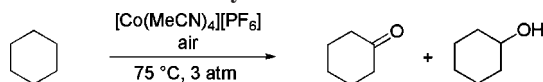
Scheme 5. Polymerization of Styrene[a][118]
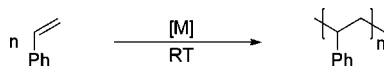
[a] [M] = [Co(MeCN)$_6$][(BF$_4$)]$_2$, [Ni(MeCN)$_6$][(BF$_4$)]$_2$.
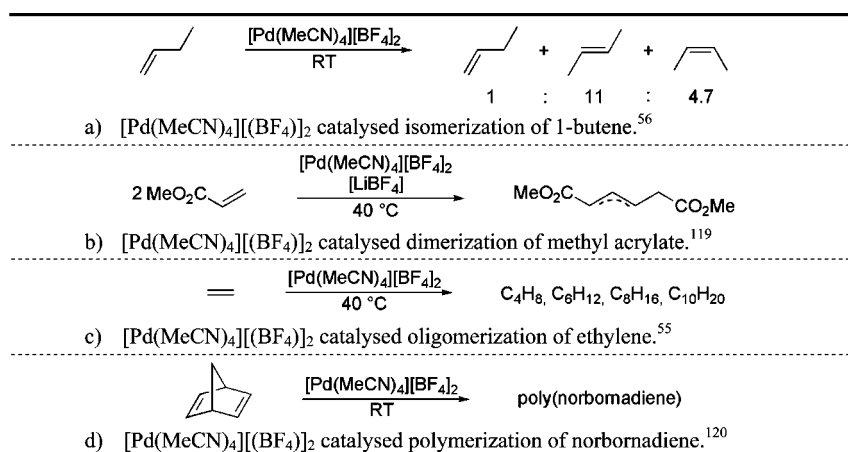
available in three dimensions, MCM-48 is in many cases more useful than the one-dimensional MCM-41.

Like commonly used silica and alumina supports, the inner surfaces of MCM-41 and MCM-48 are covered with silanol groups, which enable the immobilization of transition metal complexes by direct grafting. The quadruply bonded dimolybdenum complex salt [Mo$_2$(MeCN)$_{10}$][BF$_4$]$_4$, for example, reacts with purely siliceous MCM-41 in acetonitrile to give a composite material in which solvent-stabilized cationic molybdenum fragments are isolated and well-dispersed on the silica surface (see Figure 8).[147,150]

The structural integrity of the substrate was confirmed by powder XRD and N$_2$ adsorption studies. ^{13}C CP-MAS NMR

and FTIR 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 concluded from X-ray absorption fine structure spectroscopy (XAFS) that the Mo−Mo quadruple bond is retained in the grafted species and that no significant change occurs in the ligands surrounding the [Mo−Mo]$^{4+}$ core. Furthermore it has been suggested that the complex undergoes only weak monopodal anchoring to the silica surface. These examinations shed new light on the previously described findings of McCann et al.[3,134,135] and answer the question whether the Mo−Mo bond is retained or not. In the derivatized material, the surface coverage of Mo atoms is 0.18 nm^{-2}, slightly lower than the value for the concentration of free hydroxyl groups on the surface of pure MCM-41. The incompleteness of the loading might be due to steric crowding of the complexes, which may prevent reaction with all of the surface silanol sites. ^{29}Si CP-MAS NMR shows 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 5−10 Å. The supported [Mo$_2$(MeCN)$_{10}$][BF$_4$]$_4$ complex is highly air sensitive. Mo K-edge EXAFS confirms that air

Table 9. Utilization of Pd Complexes

a)   [Pd(MeCN)$_4$][(BF$_4$)]$_2$ catalysed isomerization of 1-butene.[56]

b)   [Pd(MeCN)$_4$][(BF$_4$)]$_2$ catalysed dimerization of methyl acrylate.[119]

c)   [Pd(MeCN)$_4$][(BF$_4$)]$_2$ catalysed oligomerization of ethylene.[55]

d)   [Pd(MeCN)$_4$][(BF$_4$)]$_2$ catalysed polymerization of norbornadiene.[120]

Scheme 6. Coupling of Phenylacetylene with an Aldehyde (R^2 = Aryl) and a Dialkylamine (R^1 = H, Me) Catalyzed by Silver(I) Complexes^a.[97]
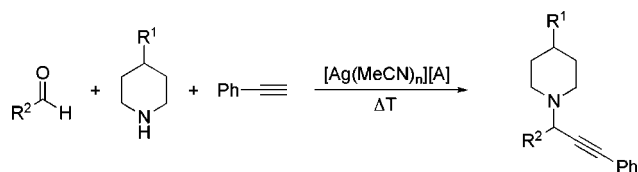
^{a} n = 2, A = B(C$_6$H$_3$(CF$_3$)$_2$)$_4^-$; n = 4, A = B(C$_6$F$_5$)$_4^-$, (C$_6$F$_5$)$_3$B−C$_3$H$_3$N$_2$−B(C$_6$F$_5$)$_3^-$.

Scheme 7. Dimerization of 2-Methylbut-2-ene Catalyzed by [Pt(MeCN)$_4$][BF$_4$]$_2$[99]
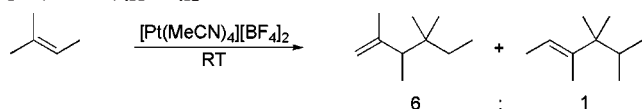
oxidation results in the formation of a surface-fixed dioxo-bridged binuclear species. The heterogenized complex was tested for the polymerization of methylcyclopentadiene at room temperature. A polymer yield of 7.2% was achieved after 16 h.[147,150]

[Rh$_2$(MeCN)$_{10}$][BF$_4$]$_4$ is another binuclear complex salt that has been heterogenized in MCM-41. As in the case of the molybdenum dimer, the spectroscopic assay suggests retention of equatorially coordinated acetonitrile groups, but loss of weakly bonded axial groups, pointing toward immobilization by interaction with surface silanol groups in the axial position. As found for the supported Mo complex, the surface coverage of Rh atoms is 0.18 nm^{-2}. A detected weakening of the Rh−Rh bond explains why the immobilized dinuclear complexes exhibit enhanced sensitivity to cleavage of the metal−metal bond, either by photodissociation or by reaction with free silanol groups on the silica surface (see Scheme 9). Unlike the results found for the unsupported complex, the formation of monomeric species is irreversible for the supported moieties.[151]

Several monometallic acetonitrile complexes [M^{II}-(MeCN)$_4$][BF$_4$]$_2$ (M = Mn, Fe, Co, Ni, Cr, and Zn) were also reacted with purely siliceous MCM-41 in acetonitrile to yield composed materials in which solvent-stabilized cationic metal centers are isolated and well-dispersed on the silica surface (see Table 15).[152]

Powder XRD and N$_2$ adsorption studies attest retained textural properties of the mesoporous host throughout the grafting process. FTIR spectroscopy indicates that the mechanism of surface attachment possibly involves a weak interaction of the metal complex with single silanol groups at the MCM surface.[152]

A further possibility to heterogenize an acetonitrile complex in MCM-41 was described later, when [Mn-(MeCN)$_4$][B(C$_6$F$_5$)$_4$]$_2$ was immobilized in MCM-41 that had been derivatized with a pyrazolpyridine ligand (see Scheme 10).[106]

N$_2$ adsorption and IR/Raman spectroscopy of the derivatized material confirm that the textural properties of the host were preserved during the grafting experiment and that the channels remain accessible. A metal loading of 0.72 wt % (0.13 mol g^{-1}) can be measured, indicating about one-third of the pyrazolylpyridine groups in MCM-41-PP are coordinated to manganese centers.

In contrast to the complexes that were immobilized by direct grafting with purely silicic MCM-41 and whose charge is reduced after immobilization, the overall charge of the complexes being immobilized in derivatized MCM-41 is maintained.

The use of a bidentate ligand also diminishes leaching of the Mn(II) species in comparison to a monodentate surface-fixed donor ligand. However, not unexpectedly, the additional electron density given by a bidentate Lewis base ligand reduces the catalytic activity of the cation significantly.[142]

The activity of transition metal nitrile cations declines in all of the above-described cases for cyclopentadiene polymerization when fixed to surfaces, this being most likely due to the reduction of its Lewis acidity. Ionic grafting was thought to provide a way around these problems. Therefore, the metal complexes were grafted on 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 11).

With this method, the cation and one of the noncoordinating anions remain largely unchanged. Currently, three different systems are known from the literature: [Mn(MeCN)$_6$][B(C$_6$F$_5$)$_4$]$_2$ grafted on H-AlMCM-41/48 or Na-AlMCM-41/48[142] and [Cu(MeCN)$_6$][B(C$_6$F$_5$)$_4$]$_2$,[115] as well as [Cu(MeCN)$_4$][BF$_4$]$_2$[111] heterogenized on Na-AlMCM-41 or Na-AlMCM-48.

The grafted [Cu(MeCN)$_4$][BF$_4$]$_2$ (copper content 1.6 wt %) 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-
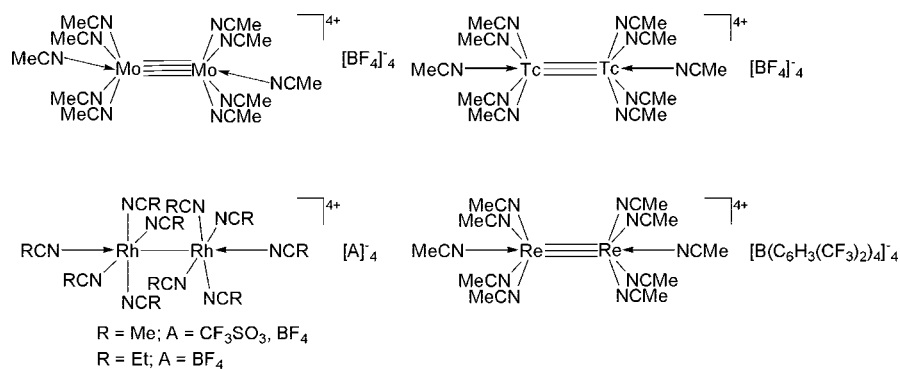
Figure 5. Known structures of dimeric metal(II) complexes.[88,125,129,130,132]

Table 10. Dimeric Transition Metal Complexes

element	cation	anion		
		BF_4^-	$CF_3SO_3^-$	$B(C_6H_3(CF_3)_2)_4^-$
Mo	$[Mo_2(MeCN)_8]^{4+}$		$+^{29}$	
	$[Mo_2(MeCN)_{10}]^{4+}$	$+^{130}$		
Tc	$[Tc_2(MeCN)_{10}]^{4+}$	$+^{129}$		
Rh	$[Rh_2(MeCN)_{10}]^{4+}$	$+^{88,125,131}$	$+^{88}$	
	$[Rh_2(EtCN)_{10}]^{4+}$	$+^{88}$		
Re	$[Re_2(MeCN)_8]^{4+}$	$+^{128}$		
	$[Re_2(MeCN)_{10}]^{4+}$	$+^{132}$		$+^{132}$

Table 11. IR Data of Selected Dimeric Complexes

compound	$\nu(CN)$ [cm^{-1}]	matrix	ref
$[Mo_2(MeCN)_{10}][BF_4]_4$	2247 (vs)/2306 (w)/2276 (w) 2293 (s)/2338 (m)/2293 (s) 2325 (m)/2360 (s)/2322 (m) x/x/2359	Nujol/solution (MeCN)/KBr	127/130/144
$[Mo_2(MeCN)_8][CF_3SO_3]_4$	2295 2320	Nujol	29
$[Tc_2(MeCN)_{10}][BF_4]_4$	2302 2330	Nujol	129
$[Rh_2(MeCN)_{10}][BF_4]_4$	2300 (w) 2317 (m) 2342 (m)	Nujol, CsI	88, 125, 126
$[Rh_2(EtCN)_{10}][BF_4]_4$	2287 (m) 2324 (s)	Nujol, CsI	88
$[Rh_2(MeCN)_{10}][CF_3SO_3]_4$	2286 (m) 2316 (w) 2345 (m)	Nujol, CsI	88
$[Re_2(MeCN)_8][BF_4]_4$	2295 (w) 2328 (m)	KBr	128

Table 12. ^{1}H NMR Data ($T = 22$ °C) of Selected Dimeric Complexes

compound	δ [ppm]	solvent	reference
$[Mo_2(MeCN)_{10}][BF_4]_4$	1.95 (s)	CD$_3$CN	127, 130
$[Mo_2(MeCN)_8][CF_3SO_3]_4$	1.55 (s)/1.95 (s)	C$_3$D$_6$O/CD$_2$Cl$_2$	29/18
$[Tc_2(MeCN)_{10}][BF_4]_4$	2.95 (s) 1.95 (s)	CD$_3$CN	129
$[Rh_2(MeCN)_{10}][BF_4]_4$	2.65 (s) 1.95 (s)	CD$_3$CN	88, 126
$[Rh_2(MeCN)_{10}][CF_3SO_3]_4$	2.79 (s) 2.02 (s)	CD$_3$NO$_2$	88
$[Rh_2(EtCN)_{10}][BF_4]_4$	3.03 (q) 2.35 (q) 1.36 (t) 1.19 (t)	CD$_3$CN	88

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 (see Table 16). The activity reduction after the first run could be due to initial partial leaching of more weakly bonded complexes. A further

factor might be the absorption of reactant/product molecules on the active species of the surface, as already discussed above.

Different results are obtained when another copper complex, $[Cu(MeCN)_6][B(C_6F_5)_4]_2$, is tested for aziridination (see Table 17).[115] The example given in Table 17 shows that it is seemingly possible for certain immobilized catalysts to achieve higher product yields than with the respective homogeneous catalysts. Again, the grafted Na-AlMCM-48 catalyst (copper content 2.0 wt %) leads to better results than the one grafted on Na-AlMCM-41 (copper content 1.0 wt %), and the catalysts can be reused several times. In further aziridination reactions, the heterogeneous catalysts generate yields of the same order of magnitude as in the case of the homogeneous systems.

The complex $[Mn(MeCN)_6][B(C_6F_5)_4]_2$ grafted on Na-AlMCM41/48 (manganese content 0.5−0.6 wt %) shows higher catalytic activity for the polymerization of 2-methyl propene (6−8% product yield) than the samples prepared on H-AlMCM41/48 (manganese content 0.25−0.3 wt %; 3−5% product yield). The presence of less Mn in the

Table 13. Selected Bond Lengths and Bond Angles of Dimeric Complexes

|	distance [Å]		angle [deg]		
complex	M—M	M—N	N—M—N	M—M—N	ref
[Mo$_2$(MeCN)$_{10}$][BF$_4$]$_4$	2.187(1)	2.141(9)	80.5(4)	101.8(3)	130
		2.138(10)	79.2(4)	98.1(3)	
		2.123(9)	80.2(4)	97.6(3)	
		2.113(10)	82.7(4)	100.2(3)	
		2.600(13)[a]	87.4(4)		
			160.4(4)		
			86.1(4)		
			92.2(4)		
			161.5(4)		
			88.3(3)		
[Rh$_2$(MeCN)$_{10}$][BF$_4$]$_4$	2.624(1)	1.986(4)		90.2(1)	88,125
		1.980(4)		178.1(1)	
		1.995(4)			
		1.985(4)			
		2.191(5)[a]			
[Rh$_2$(EtCN)$_{10}$][BF$_4$]$_4$	2.604(9)	1.991(4)		91.2(1)	88
		1.977(4)		176.9(2)	
		1.982(4)			
		1.987(4)			
		2.180(6)[a]			
[Rh$_2$(MeCN)$_{10}$][CF$_3$SO$_3$]$_4$	2.616(2)	2.01(1)		88.7(3)	88
		1.97(1)		179.0(4)	
		2.15(1)[a]			
		1.96(1)			
		2.03(1)			
		2.14(1)[a]			
[Re$_2$(MeCN)$_{10}$][B(C$_6$H$_3$(CF$_3$)$_2$)$_4$]$_4$·4CH$_2$Cl$_2$·CH$_3$CN	2.263(4)	2.410(5)[a]	89.3(2)	97.0(17)	132
		2.058(6)	88.5(2)	99.5(16)	
		2.062(7)	164.5(2)	176.8(14)	
		2.045(6)	82.3(2)	96.9(17)	
		2.060(6)	81.2(2)	98.5(16)	
		2.375(5)[a]	163.5(2)	95.5(17)	
		2.070(7)	87.2(2)	96.9(17)	
		2.075(7)	90.6(2)	176.5(16)	
		2.052(7)	80.0(2)		
		2.054(7)	167.6(2)		
			83.3(2)		
			84.3(2)		

[a] Axial ligand.

H-AlMCM41/48 samples is attributed to the weak-to-moderate Brønsted acidic nature of H-AlMCM41/48. The lower activity of the Mn/H-AlMCM41/48 systems is most likely due to the presence of additional protons on the surface, influencing the (cationic) polymerization process negatively.[142]
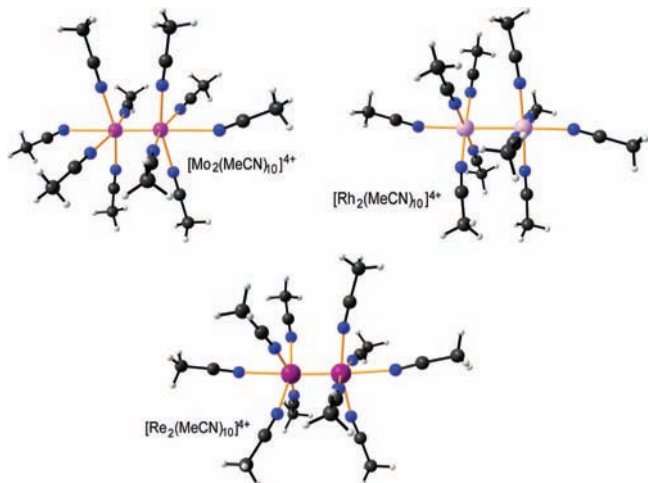
Figure 6. PLATON drawings of the [M$_2$(MeCN)$_{10}$]$^{4+}$ cores in [Mo$_2$(MeCN)$_{10}$][BF$_4$]$_4$·2MeCN, [Rh$_2$(MeCN)$_{10}$][BF$_4$]$_4$, and [Re$_2$(MeCN)$_{10}$][B(C$_6$H$_3$(CF$_3$)$_2$)$_4$]$_4$·4CH$_2$Cl$_2$·MeCN.[88,130,132]

Table 14. Selected Bond Lengths and Bond Angles of [Rh(MeCN)$_4$(BF$_4$)$_{1.5}$]$_\infty$[27,88]

distance [Å]		angle [deg]	
Rh—Rh	Rh—N	N—Rh—N	Rh—Rh—N
2.928(8)	1.991(4)	91.2(2)	177.8(2)
2.844(8)	1.985(4)	88.7(2)	88.9(11)
		176.9(2)	91.1(11)
			88.4(11)
			91.6(11)

Scheme 8. Polymerization of Phenylacetylene (Top) and Ring-Opening Metathesis Polymerization of Norbornene (Bottom)
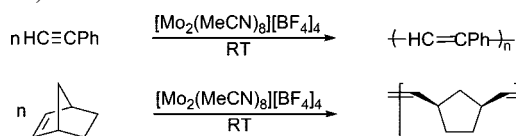
A recently published work[143] elaborates on the immobilization of the anion instead of the cation (see Scheme 12).

The activities of different heterogeneous samples were examined in the cyclopropanation of styrene and compared with the activity of homogeneous [Cu(NCMe)$_6$][B(C$_6$F$_5$)$_4$]$_2$ (CuA$_2$) in the same reaction (see Table 18).[143]

The heterogeneous materials show a lower activity for cyclopentadiene polymerization than the complexes in
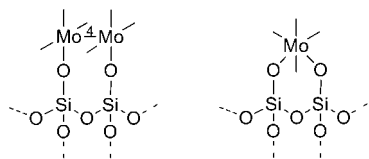
Figure 7. Anchoring of a dimolybdenum(II,II) complex onto a silica surface: left bipodal anchoring; right, anchoring after rupture of the Mo–Mo bond).
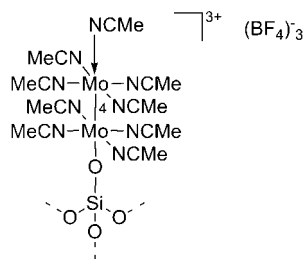
Figure 8. Monopodal anchoring of $[Mo_2(MeCN)_{10}][BF_4]_4$ on MCM-41.

Scheme 9. $[Rh_2(L)_{10}][BF_4]_4$ on MCM-41 (L = MeCN) before and after Photodissociation[151]
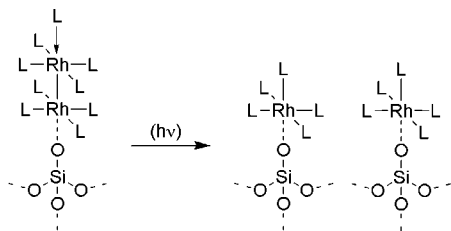
Table 15. Textural Parameters of MCM-41-Supported $[M(MeCN)_4][BF_4]_2$ Samples and Catalytic Results with Them as Initiators for the Polymerization of Cyclopentadiene[a][152]

MCM-41/M^{II}	S_M[b] (atoms/nm²)	PY[c] (%)
MCM-41/Cr	0.23	8.3
MCM-41/Fe	0.33	6.7
MCM-41/Co	0.26	5.0
MCM-41/Zn	0.30	11.6

[a] Reaction time = 16 h; temperature = 25 °C; solvent = methylene chloride. [b] S_M = approximate metal atom surface coverage. [c] PY = polymer yield.

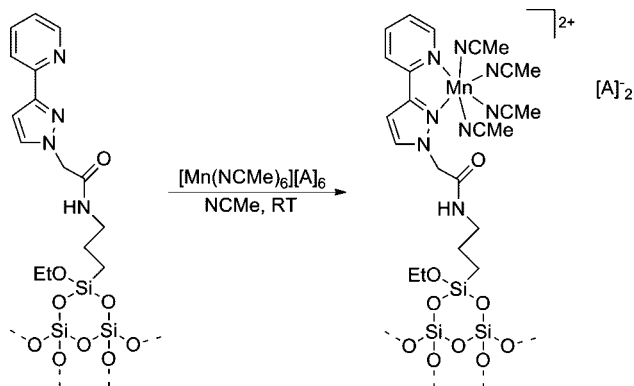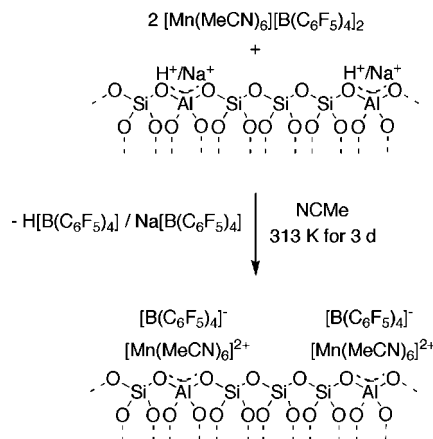**Scheme 10. Synthesis of MCM-41-PP/Mn [A = B(C$_6$F$_5$)$^{4-}$][106]**

Scheme 11. Anchoring of $[Mn(MeCN)_4][B(C_6F_5)_4]_2$ on a Mesoporous Silica Surface[142]

Table 16. Cyclopropanation of Cyclooctene with Supported and Unsupported $[Cu(MeCN)_4][BF_4]_2$ Using EDA[111]

complex	run	yield[a] (%)
$[Cu(MeCN)_4][BF_4]_2$		42
Na-AlMCM-48/Cu	1	38
	2	19
	3	19
Na-AlMCM-41/Cu	1	18
	2	12
	3	11

[a] Based on EDA (ethyl diazoacetate) conversion; reaction time = 20 h; temperature = 25 °C; solvent = acetonitrile.

Table 17. Catalytic Aziridination of Styrene with Supported and Unsupported $[Cu(MeCN)_6][B(C_6F_5)_4]_2$ Using PhI=NTs[115]

catalyst	run	yield[a] (%)
$[Cu(MeCN)_6][B(C_6F_5)_4]_2$		45
Na-AlMCM-48/Cu	1	65
	2	62
	3	56
Na-AlMCM-41/Cu		50

[a] Based on PhI=NTs conversion; reaction time = 20 h; temperature = 30 °C; solvent = acetonitrile.

homogeneous phase. This might be due to the substrate encountering greater difficulty in reaching the growth sites of the polymers. Another explanation could be that some polymer molecules get stuck in the pores of MCM-41. That the polymer finally covers the surface of the carrier material to a large extent may also be possible. No further evidence supporting one of these hypotheses has been presented to date, however. Furthermore, the activity of the immobilized complex decreases until the second or third run but remains stable afterward. The decrease in activity may be again due to the adsorption of reactant or product molecules in the channels of the mesoporous material and, perhaps to a minor extent, decomposition.[143]

Another carrier material tested for heterogenization is SBA-15. Among those that have been examined, this is the mesoporous material with by far the largest pore size. It has highly ordered hexagonally arranged meso channels, with thick walls, adjustable pore sizes from 3 to 30 nm, and a high chemical and thermal stability.[153,154]

The copper complex $[Cu(MeCN)_6][B\{C_6H_3(m\text{-}CF_3)_2\}_4]_2$ was grafted on the surface of aminosilane-modified SBS-15 molecular sieve (see Figure 9).[155]

SBA-15 materials exhibit a narrow pore size distribution. The theoretical value of silanol groups present in SBA-15 materials that were synthesized under similar conditions is 4 nm⁻¹. One third of these silanol moieties have reacted with the aminosilane linkers. The surface coverage of Cu atoms is 0.22 nm⁻².

Scheme 12. Anchoring of [Cu(NCMe)$_6$][B(C$_6$F$_5$)$_4$]$_2$ on Modified MCM-41[143]
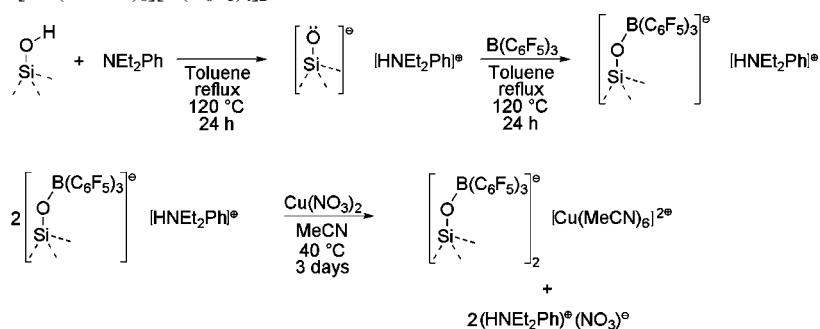
Table 18. Catalytic Cyclopropanation of Styrene with Various Materials Using EDA[143]

catalyst	run	yield^a (%)	selectivity(cis/trans)
[Cu(NCMe)$_6$][B(C$_6$F$_5$)$_4$]$_2$		79	32:68
MCM-41		0	
MCM-41-HNEt$_2$Ph		<5	
MCM-41-CuA$_2$	1	57	45:55
	2	46	45:55
	3	42	41:59
	4	42	41:59

^{a} Based on EDA (ethyl diazoacetate) conversion; reaction time = 24 h; temperature = 25 °C; solvent = acetonitrile.
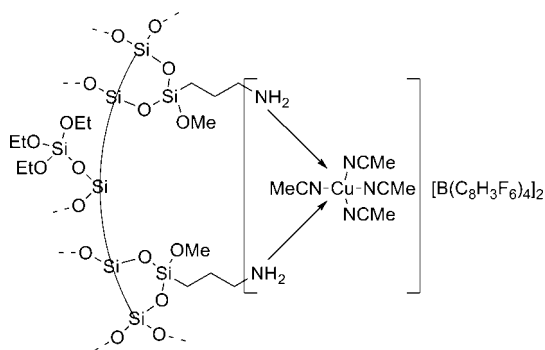

Figure 9. SBA-15-SNH$_2$CuA$_2$.[155]

Table 19. Benzaldehyde Olefination with Supported and Unsupported [Cu(MeCN)$_6$][B{C$_6$H$_3$(m-CF$_3$)$_2$}$_4$]$_2$[a155]

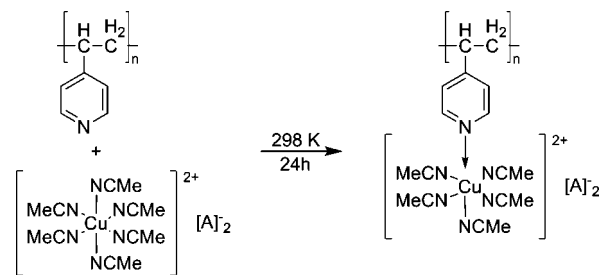| catalyst	run	yield (%)
[Cu(MeCN)$_6$][B{C$_6$H$_3$(m-CF$_3$)$_2$}$_4$]$_2$		12.1
SBA-15-SNH$_2$CuA$_2$	1	44.3
	2	36.0
	3	35.1

^{a} Reaction time = 24 h; temperature = 80 °C.

Both the homogeneous and the heterogeneous complexes were tested for aldehyde olefination reactions. The achieved yields of the olefination of benzaldehyde are given in Table 19.[155]

The heterogeneous complexes show, according to the published results, even better performance in several reactions than their homogeneous counterparts. That observation is ascribed to the uniform distribution and site isolation of the active sites on the surface.[143]

4.2. Anchoring to Polymers

The development of polymer-supported catalysts that have easily accessible complexing functionalities, allowing both stability and uniformity of the obtained materials, is a great achievement.[156] Several types of polymers that have pyridine

Scheme 13. Immobilization of [Cu(MeCN)$_6$][A]$_2^a$ on Poly(4-vinylpyridine)[159]

^{a} A = B(C$_6$F$_5$)$_4^-$, B(C$_6$H$_3$(CF$_3$)$_2$)$_4^-$.

Table 20. Cyclopropanation of Cyclooctene with Supported and Unsupported [Cu(MeCN)$_6$][A]$_2$ (A= B(C$_6$F$_5$)$_4^-$, B(C$_6$H$_3$(CF$_3$)$_2$)$_4^-$) Using EDA[159]

catalyst	run	yield^a (%)
[Cu(MeCN)$_6$][B(C$_6$F$_5$)$_4$]$_2$		37
[Cu(MeCN)$_6$][B{C$_6$H$_3$(m-CF$_3$)$_2$}$_4$]$_2$		48
P4VP-a	1	58
	2	56
	3	30
P4VP-b	1	63
	2	59
	3	28

^{a} Based on EDA conversion; reaction time = 24 h; temperature = 25 °C; solvent = acetonitrile.

donor (N-donor) groups such as poly(4-vinylpyridine) (P4VP) have been examined to create stable carrier−catalyst interactions.[138] The synthesis of P4VP-supported metal(II) complexes is based on the donor−acceptor interaction between the pyridine nitrogen atoms and the metal center, where the nitrogen atom of the pyridine ring acts as a proton acceptor.[157,158]

In 2006, the two copper complexes [Cu(MeCN)$_6$][B{C$_6$H$_3$(m-CF$_3$)$_2$}$_4$]$_2$ and [Cu(MeCN)$_6$][B(C$_6$F$_5$)$_4$]$_2$ were described as having been immobilized on poly(4-vinylpyridine) (see Scheme 13).[159]

The obtained copper loading of the two complexes grafted on P4VP shows that a higher amount of complex [Cu(MeCN)$_6$][B(C$_6$F$_5$)$_4$]$_2$ (a) is grafted (0.9 wt %) than of complex [Cu(MeCN)$_6$][B{C$_6$H$_3$(m-CF$_3$)$_2$}$_4$]$_2$ (b) (0.8 wt %). Nevertheless, complex P4VP-b has almost always a higher activity in cyclopropanation reactions than complex P4VP-a. In the case of cyclopropanation of cyclooctene, the activity of both immobilized catalysts is even higher than that of the unsupported ones, and they remain active for several runs (see Table 20).[159] The decreasing product yield, however, might, at least in part, be due to catalyst leaching.

5. Conclusion

Transition metal complexes bearing weakly coordinating counteranions and being stabilized by labile nitrile ligands could be applied as good starting materials for the synthesis of a variety of other materials and complexes. It emerged during the past decade that the compounds are comparatively easy to handle and sufficiently straightforward spectroscopic methods, such as vibrational or UV−vis spectroscopy, are at hand to ensure the cleanness of the complexes when used in reactions or as catalysts. Among the synthetic applications, the generation of molecular wires, starting from both monomeric and dimeric compounds, seems to be particularly interesting. A use as building blocks in metal− organic frameworks (MOFs), being increasingly attractive these days, may also arise shortly. Furthermore, several of the title complexes are applicable as catalysts for several organic reactions, among them polymerization reactions in both the homogeneous and heterogeneous phase. Since the heterogenization of the complexes opens the possibility of recycling the catalysts and, so far, the catalytic activities of supported catalysts are in most cases quite low compared with their activities in the homogeneous phase, much work has still to be dedicated to finding a better way of immobilizing the catalyst compounds. Additionally, work is necessary to understand the mechanisms of the catalyzed reactions and the role of the counteranions.

Considering the composition and straightforward synthesis of the solvent-stabilized transition metal complexes, it is assumed that more knowledge about several of the catalyzed reactions might be gained by a closer examination of the catalysts. Such knowledge could facilitate the discovery of other, highly efficient catalysts and may even help to employ cheaper, more energy-efficient, and environmentally benign industrial reactions. In addition to experimental work, theoretical calculations might be very helpful to shed more light on the reaction mechanisms in which solvent-stabilized transition metal cations with weakly coordinating anions are involved.

6. Acknowledgments

7. References

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