DOI: 10.1002/ejic.200800201

# Synthesis and Characterization of Acetonitrile-Ligated Transition-Metal Complexes with Tetrakis(pentafluorophenyl)borate as Counteranions

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**Keywords:** Acetonitrile ligands / Weakly coordinating anions / Transition metals

Complexes with the general formula $[M^{II}(NCCH_3)_6][TPFB]_2$ [M = Cr, Fe, Co, Ni, Cu, Zn, $(TPFB)^-$ = tetrakis(pentafluorophenyl)borate] were synthesized and characterized both in the solid state and in solution. According to the spectroscopic data, [TPFB] can be considered as a truly noncoordinating anion. The $NCCH_3$ ligands are lost if the samples are kept at room temperature for extended periods of time. Thermolysis leads to the loss of the $NCCH_3$ ligands and decomposition of the anion above 100 °C with the formation of $MF_2$. It has to be noted that distortion of the geometries of the $Cu^{II}$, $Zn^{II}$ and $Cr^{II}$ complexes occurs, as evidenced by infrared spectroscopy. The complexes can be easily prepared and obtained in high yields and are moderately sensitive to air.


## Introduction

First-row transition-metal complexes with the general formula $[M(NCCH_3)_6][A]_2$ ($M^{II}$ = Cr, Mn, Fe, Co, Ni, Cu, Zn; A = counteranion) and some of their dimeric second- and third-row congeners with the formula $[M_2(NCCH_3)_{8-10}][A]_2$ ($M^{II}$ = Mo, Tc, Re, Rh; A = counteranion) have been known for many years.[1,2] Several groups have contributed to their synthesis. These complexes are synthetically important as starting materials, and some of these 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 anions (weakly coordinating anions) 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 with the general formula $M(NCCH_3)_x^+$-$(M'Cl_4)_y^-$.[4] In order to obtain acetonitrile-ligated compounds, all reactions have to be carried out in nitrile solutions.

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It has been 30 years since the term "noncoordinating anion"[5] was coined to describe anions such as $ClO_4^-$, $NO_3^-$ and $BF_4^-$, which usually do not coordinate (or coordinate weakly) in aqueous solution. In the last three decades, a plethora of species that closely resemble noncoordinating anions has been synthesized. In many cases they are actually weakly coordinating ("weakly coordinating anions", WCAs). 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 multiple well-established applications, e.g. 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 at oxidation potentials that are not too high.[7] Furthermore, transition-metal salts of WCAs are also found.[7] 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 such as $B(C_6F_5)_3$ produces the tight ion pair $[Cp_2MMe]^+[MeB(C_6F_5)_3]^-$.[8] WCAs can also be introduced into a system through metathesis reactions between $M^+[X]^-$ ($[X]^-$ = WCA, M = univalent metal, such as Li, Na, K, Ag, Tl) and 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. Silver nitrate has been used as a standard testing reagent to differentiate between free and complexed chloride for a long time. 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

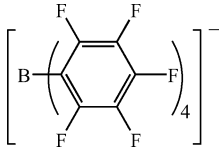
ion abstraction from labile sources. For the synthesis of versatile types of luminescent heterometallic materials in supramolecular chemistry, compounds of the type $[M(NCCH_3)_4][A]$ (M = Ag; A = $BF_4^-$, $PF_6^-$, $ClO_4^-$, etc.) have been utilized as starting materials.[9] Complexes with the general formula $[M(NCCH_3)_{2-6}][A]_{1-2}$ can be used as catalysts in the cationic polymerization of cyclopentadiene and methylcyclopentadiene in both a 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 = $B(C_6F_5)_4^-$, $B\{C_6H_3(m\text{-}CF_3)_2\}_4^-$, and $\{(C_6F_5)_3B\text{-}C_3H_3N_2\text{-}B(C_6F_5)_3\}^-$, with excellent activities for the polymerization of isobutene has been reported.[11]

In this work, the synthesis and characterization of complexes, with the 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 in solution is reported, together with a brief report on the catalytic behaviour of these compounds.

## Results and Discussion

### Synthesis and 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)] to form the corresponding potassium salt. The potassium salt was then transformed into the silver salt by reaction with silver nitrate [Equation (1d)].



Scheme 1.

$$R\text{–}Br + n\text{BuLi} \xrightarrow[-78\ ^\circ C]{Et_2O} RLi + n\text{BuBr} \quad (1a)$$

$$4\ RLi + BCl_3 \xrightarrow[-78\ ^\circ C]{} Li[B(R)_4] + 3\ LiCl \quad (1b)$$

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

$$K[B(R)_4] + AgNO_3 \xrightarrow[r.t.]{CH_3CN} Ag[B(R)_4] + KNO_3 \quad (1d)$$

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 stable in air and can therefore be handled under normal atmospheric conditions 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).

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

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

X = Cl, Br

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

### Infrared Spectroscopic Analysis

The infrared (IR) spectra of the complexes recorded in a KBr matrix exhibit two sharp $\nu$(CN) absorptions of medium intensity [assigned to the fundamental $\nu_2$(CN) stretching mode and a combination of the modes ($\nu_3$ + $\nu_4$)][1x] at approximately 2325 and 2295 $cm^{-1}$, respectively, as shown in Table 1.

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.

| Metal | Anion, A | $\nu$(CN) [$cm^{-1}$] | | | Ref. |
|---|---|---|---|---|---|
| Cr | [TPFB] | 2305 | 2278 | | [a] |
| | [TFPB] | 2324 | 2297 | 2277 | [1x] |
| | $[BF_4]$ | 2333 | 2305 | | [3a] |
| Fe | [TPFB] | 2314 | 2284 | | [a] |
| | [TFPB] | 2318 | 2291 | | [1x] |
| | $[BF_4]$ | 2310 | 2287 | | [1c] |
| Co | [TPFB] | 2322 | 2296 | | [a] |
| | [TFPB] | 2321 | 2295 | | [1x] |
| | $[BF_4]$ | 2316 | 2292 | | [1c] |
| Ni | [TPFB] | 2326 | 2300 | | [a] |
| | [TFPB] | 2326 | 2299 | | [1x] |
| | $[BF_4]$ | 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(pentafluorophenyl)borate, TFPB = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate.

There are, however, two 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 has already been observed for the related complex $[Cr^{II}(NCCH_3)_6][TFPB]_2$ {TFPB = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate};[1x] however, it is absent in the spectra of the $Cr^{II}$ compound described here. This three-peak absorption pattern is assigned to the presence of two slightly more weakly coordinating "axial" acetonitrile ligands (relative to the four "equatorial" acetonitrile ligands). This, however, seems unlikely for the $Zn^{II}$ complex. This assumption might also explain the lower energy of the vibration of the $Cr^{II}$ complex relative to that of the other complexes, although no third vibration was observed.

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

When these compounds are kept at room temperature for prolonged periods of time, one or two acetonitrile ligands are lost, according to the elemental analysis data. However, the complexes can be obtained with 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]

### Thermogravimetry

Thermogravimetric analysis (TGA) was performed on all compounds. The onset of the first decomposition step for the Cu complex occurs at ca. 107 °C and is associated with a mass loss of 18.4 wt.-%. Since an analogous decomposition step cannot be found in acetonitrile-free $K[B(C_6F_5)_4]$, this mass loss is likely to correspond to 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 the Fe complex and is associated with a loss of 13.1 wt.-% at 107.8 °C. The Cr and Zn complexes show a 4.1 wt.-% and 4.0 wt.-% mass loss at 109.6 °C and 105.7 °C, respectively. These decomposition steps correspond to the loss of two acetonitrile ligands (4.9 wt.-%) in each case. Both complexes also show the loss of a second acetonitrile at 160.7 °C {5.7 wt.-% [two $NCCH_3$ ligands (4.9 wt.-%)]} and 178.3 °C {10.4 wt.-% [four $NCCH_3$ ligands (9.8 wt.-%)]}, respectively. The first decomposition steps of the Co and Ni complexes occur above 200 °C and account for ca. 78.2 wt.-% and 71.3 wt.-% mass loss, respectively. Accordingly, these steps must account for the losses of all acetonitrile ligands and for anion fragmentation. The Ni complex has the highest thermal stability, while the Zn complex has the lowest thermal stability of all the compounds examined. The decomposition behaviour of the Mn complex was reported earlier.[11] Its first decomposition step occurs at 178.5 °C, which corresponds to a 14.0 wt.-% loss accounting for the loss of all six $NCCH_3$ ligands (14.1 wt.-%). The second decomposition step is observed at 260.3 °C 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.

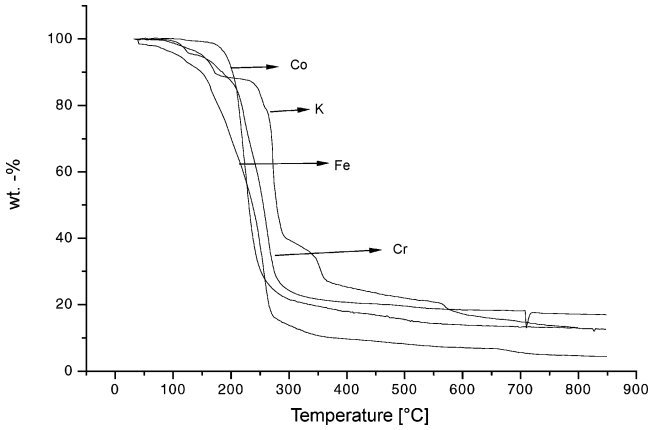



Figure 1. TGA of the K[TPFB] and $[M^{II}(NCCH_3)_6][TPFB]_2$ complexes, [M = Co, Fe, Cr].

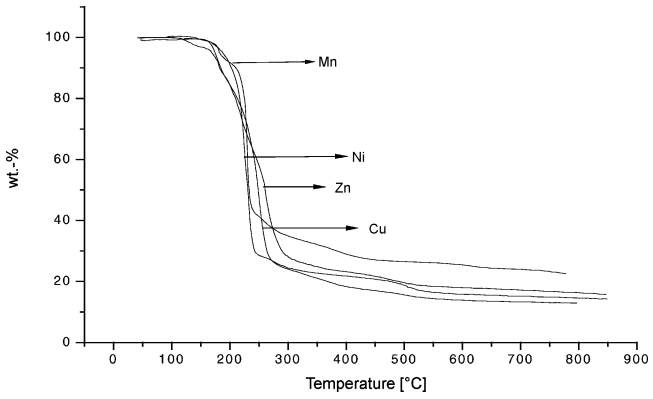



Figure 2. TGA of the $[M^{II}(NCCH_3)_6][TPFB]_2$ complexes, [M = Mn, Ni, Zn, Cu].

The Fe complex looses the highest relative mass within the examined temperature interval. The total weight loss observed is ca. 95 wt.-%, which correlates 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 decomposition of the other complexes is incomplete. For purposes of comparison with another noncoordinating counteranion, Table 3 presents the TGA results of $[M^{II}(NCCH_3)_6][TFPB]_2$.[1x] {M = Ni, Co, Fe, Mn, Cr, V, [TFPB] = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate}.

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 °C/min.

| Metal | $T_{onset}$ [°C] | wt.-% loss | $T_{onset}$ [°C] | wt.-% loss | $T_{onset}$ [°C] | wt.-% loss | $T_{onset}$ [°C] | wt.-% loss | $T_{onset}$ [°C] | wt.-% loss | Total wt.-% 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 |

Table 3. Thermogravimetric analyses of $[M(NCCH_3)_6][B\{(C_6H_3)(m\text{-}CF_3)_2\}_4]_2$[1x] 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 wt.-% loss |
|---|---|---|---|---|---|---|
| | $T_{onset}$ [°C] | wt.-% 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 can be seen by comparing Tables 2 and 3, there are some differences in the thermal stability of the complexes, which are seemingly dependent on the type of the noncoordinating counteranion. For the Ni complex, total decomposition is observed (95.1% wt. loss) when [TFPB] is the counteranion, while in the case of [TPFB], a residue of higher mass is obtained (85.5% wt. loss). This behaviour is different from that of the Fe complex with 95% wt. loss when [TFPB] is the counteranion. It is interesting to note that all the metal complexes coordinated with [TFPB] decompose below 100 °C with a loss of ca. one $NCCH_3$ 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 [TFPB] as the counteranion are somewhat more stable than those having [TFPB] as the counteranion.

The electronic absorption bands were measured for all complexes prepared in this work. The positions of the bands are comparable to those for the $[M^{II}(OH_2)_6]^{2+}$ ions,[13] with a shift to higher energies. This is in agreement with acetonitrile being a stronger-field ligand than water in the spectrochemical series. The molar extinction coefficients ($\varepsilon$) range from 1.0 to 49.1 $cm^{-1}\,M^{-1}$. The molar extinction coefficient values for the $[M^{II}(NCCH_3)_6]^{2+}$ ions are greater than those for the $[M^{II}(OH_2)_6]^{2+}$ ions. This is due to the increase in vibronic coupling of coordinated $NCCH_3$ relative to that for water.[12a] Table 4 shows the UV/Vis data for all the $[M^{II}(NCCH_3)_6]^{2+}[TPFB]_2^-$ complexes.

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

| Complex | Wavelength [nm] | Wavenumber [$cm^{-1}$] | Abs. | $\varepsilon$[a] [$cm^{-1}\,M^{-1}$] |
|---|---|---|---|---|
| $[Cr(NCCH_3)_6]^{2+}$ | 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 |

[a] Concentrations were between 1.5–3.0 mM in acetonitrile, pathlength 1 cm, background solvent versus solvent.

The Ni complex has three absorption bands, which is 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 band, 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 a single absorption band at 11211 $cm^{-1}$ {in comparison to $[Fe(NCCH_3)_6]^{2+}([BF_4]^-)_2$, which absorbs at 10965 $cm^{-1}$[3a] and with $[Fe(NCCH_3)_6]^{2+}([TFPB]^-)_2$, which absorbs at 10900 $cm^{-1}$}.[1x] The Cr complex shows one absorption band at 16638 $cm^{-1}$ {15500 $cm^{-1}$ for the complex $[Cr(NCCH_3)_6]^{2+}([TFPB]^-)_2$}.[1x]

The $^1H$ NMR (400 MHz, $CD_2Cl_2$, 25 °C) shifts corresponding to the methyl group in dichloromethane are observed as singlets at $\delta$ = 2.14, 2.13, 2.16 and 2.42 ppm for Ni, Zn, Cr and Fe complexes, respectively, which are slightly shifted downfield in comparison to $CH_3CN$ ($\delta$ = 1.93 ppm).[14,15]

## 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-initiators. Typical solvents are methylchloride, dichloromethane and ethene at temperatures of –80 °C or lower (–100 °C in case of ethene as solvent). Polymerization under these conditions, however, is very fast and exothermic.

Complexes with the 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

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

| Metal | Time [h] | Conversion [%] | $M_n$ [$g\,mol^{-1}$] | PDI | *exo* end groups [%] |
|---|---|---|---|---|---|
| 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 M, solvent: DCM; $c_{cat} = 0.5 \times 10^{-4}$ M, temperature: 30 °C.

advantage of these catalysts is that the reaction takes place at room temperature, and the product from these reactions have molecular weights from 0.5–5 kg mol$^{-1}$ and are colourless, honeylike viscous liquids (low-molecular-weight polyisobutene).

The polymerization reaction was carried out under these conditions at a temperature of 30 °C, with dichloromethane as solvent, a catalyst concentration of $0.5 \times 10^{-4}$ M and 2-methylpropene concentration of 1.78 M.

The Fe complex is the most-active catalyst, with conversions of up to 88% in 5 h. The average molecular weight ($M_n$) of the product polymer is 900 g mol$^{-1}$, 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. From the examination 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 of the activities for the catalysts is given in Table 5.

### 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 a more or less ideal octahedral coordination.

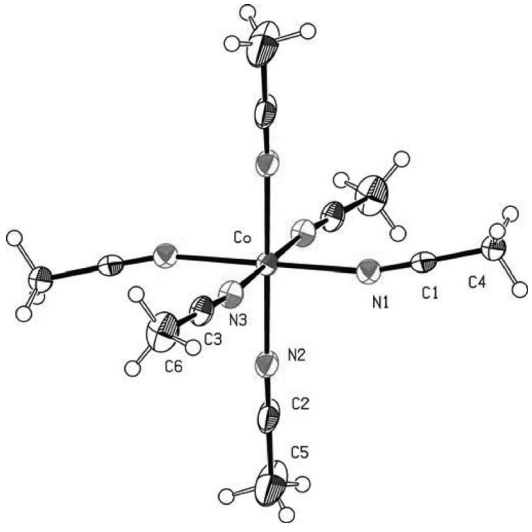



Figure 3. ORTEP plot[18f] of the dicationic part of compound **3** The cobalt atom is located on a centre of inversion. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and bond angles [°]: Co–N1 2.137(1), Co–N2 2.105(2), Co–N3 2.098(2), N1–C1 1.138(2), N2–C2 1.126(3), 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).

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 to date.

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

| | **3** |
|---|---|
| Formula | $C_{60}H_{18}B_2CoF_{40}N_6$ |
| $M_w$ [g mol$^{-1}$] | 1663.35 |
| Colour/habit | purple/fragment |
| Crystal dimensions [mm] | $0.20 \times 0.36 \times 0.51$ |
| 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) |
| $\alpha$ [°] | 69.3894(5) |
| $\beta$ [°] | 87.7262(5) |
| $\gamma$ [°] | 85.9142(5) |
| $V$ [Å$^3$] | 1573.18(2) |
| $Z$ | 1 |
| $T$ [K] | 123 |
| $D_{calcd.}$ [g cm$^{-3}$] | 1.756 |
| $\mu$ [mm$^{-1}$] | 0.439 |
| $F(000)$ | 817 |
| $\theta$ range [°] | 1.73–25.42 |
| Index ranges ($h$, $k$, $l$) | ±13, ±14, ±15 |
| No. of reflections collected | 34151 |
| No. of independent reflections/$R_{int}$ | 5780/0.033 |
| No. of observed reflections [$I > 2\sigma(I)$] | 5190 |
| No. of data/restraints/parameters | 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/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 = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

The results for the Co complex investigated in this study are in very good agreement with those reported for the corresponding complex.[17c]

## Conclusions

Complexes with the 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 FTIR spectroscopic results, it can be concluded that some of the complexes have a distorted 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. All complexes were used as catalysts for the polymerization of 2-methylpropene at room temperature. Products with molecular weights between 800 and 5300 g mol$^{-1}$ and with a high content of terminal double bonds, between 50 and 80%, are available by this reaction; the Fe compound is the most active catalyst.

## Experimental Section

All preparations and manipulations were carried out under argon by using standard Schlenk techniques. Acetonitrile was distilled from calcium hydride and kept over 3 Å molecular sieves. Unless stated otherwise, all chemicals were used as received from Aldrich. IR spectra were recorded with a Perkin–Elmer FTIR spectrometer by using KBr pellets as matrix. Thermogravimetric analyses were performed with a Netzsch TG209 system at a heating rate of 10 °C min$^{-1}$ under argon. $^1$H NMR spectroscopic measurements were performed with a Bruker AVANCE-DPX-400 spectrometer. UV/Vis spectra were recorded with a Hitachi-U3000 spectrophotometer. Solution spectra were measured in a quartz cell with a 1-cm pathlength. Elemental analyses were measured with a Vario EL metal analyzer at 1200 °C at the Mikroanalytisches Labor of the TU München. The counterion $[B(C_6F_5)_4]^-$ was prepared as described in the Results and Discussion section (see above), and the polymerization activity studies were carried out as described before.[11,16]

**$[Cr(NCCH_3)_6][B(C_6F_5)_4]_2$ (1):** $CrCl_2$ (0.08 g, 0.64 mmol) was added to a solution of $Ag[B(C_6F_5)_4]$ (1.00 g, 1.27 mmol) in dry acetonitrile (20 mL). The resulting mixture was stirred overnight in the dark. 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 greenish-yellow solid. Yield 0.65 g (61%). $C_{60}H_{18}B_2CrF_{40}N_6$ (1656.38): calcd. C 43.50, H 1.09, N 5.07; found C 43.41, H 1.04, N 4.74. Selected IR (KBr): 2305, 2278 [$\nu$(CN)].

**$[Fe(NCCH_3)_6][B(C_6F_5)_4]_2$ (2):** $FeBr_2$ (0.14 g, 0.64 mmol) was added to a solution of $Ag[B(C_6F_5)_4]$ (1.00 g, 1.27 mmol) in dry acetonitrile (20 mL). The resulting mixture was stirred overnight in the dark. 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 brownish-orange solid. Yield 0.85 g (80.0%). $C_{60}H_{18}B_2F_{40}FeN_6$ (1660.23): calcd. C 43.40, H 1.09, N 5.06; found C 43.53, H 1.09, N 4.87. Selected IR (KBr): 2314, 2284 [$\nu$(CN)].

**$[Co(NCCH_3)_6][B(C_6F_5)_4]_2$ (3):** $CoCl_2$ (0.08 g, 0.64 mmol) was added to a solution of $Ag[B(C_6F_5)_4]$ (1.00 g, 1.27 mmol) in dry acetonitrile (20 mL). The resulting mixture was stirred overnight in the dark. 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 purple solid. Yield 0.81 g (76.4%). $C_{60}H_{18}B_2CoF_{40}N_6$ (1663.32): calcd. C 43.33, H 1.09, N 5.05; found C 43.01, H 1.08, N 5.33. Selected IR (KBr): 2322, 2296 [$\nu$(CN)].

**$[Ni(NCCH_3)_6][B(C_6F_5)_4]_2$ (4):** $NiBr_2$ (0.14 g, 0.64 mmol) was added to a solution of $Ag[B(C_6F_5)_4]$ (1.00 g, 1.27 mmol) in dry acetonitrile (20 mL). The resulting mixture was stirred overnight in the dark. 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 blue–purple solid. Yield 0.83 g (78.3%). $C_{60}H_{18}B_2F_{40}N_6Ni$ (1663.08): calcd. C 43.33, H 1.09, N 5.05; found C 43.03, H 1.08, N 5.15. Selected IR (KBr): 2326, 2300 [$\nu$(CN)].

**$[Cu(NCCH_3)_6][B(C_6F_5)_4]_2$ (5):** $CuCl_2$ (0.07 g, 0.64 mmol) was added to a solution of $Ag[B(C_6F_5)_4]$ (1.00 g, 1.27 mmol) in dry acetonitrile (20 mL). The resulting mixture was stirred overnight in the dark. 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 light-green solid. Yield 0.66 g (73%). $C_{60}H_{18}B_2CuF_{40}N_6$ (1667.93): calcd. C 43.20, H 1.08, N 5.04; found C 42.98, H 1.22, N 5.09. Selected IR (KBr):2340, 2317, 2279 [$\nu$(CN)].

**$[Zn(NCCH_3)_6][B(C_6F_5)_4]_2$ (6):** $ZnCl_2$ (0.09 g, 0.64 mmol) was added to a solution of $Ag[B(C_6F_5)_4]$ (1.00 g, 1.27 mmol) in dry acetonitrile (20 mL). The resulting mixture was stirred overnight in the dark. 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%). $C_{60}H_{18}B_2F_{40}N_6Zn$ (1669.79): calcd. C 43.15, H 1.09, N 5.03; found C 42.84, H 1.34, N 5.02. Selected IR (KBr): 2324, 2297, 2267 [$\nu$(CN)].

**X-ray Crystal Determination for Compound 3:** Suitable single crystals for 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 ($\lambda$ = 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 $d_{C-H}$ = 0.98 Å and $U_{iso(H)} = 1.5U_{eq(C)}$. 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 [$I_o > 2\sigma(I_o)$], $wR2$ = 0.0719 [all data], GOF = 1.035 and shift/error < 0.001. The final difference-Fourier map shows no striking features.[18] CCDC-686893 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

## Acknowledgments

BASF AG, represented by Dr. H. M. Walter, Dr. P. Hanefeld and Dr. K. Mühlbach, is acknowledged for continuous support and interest in our research. We are grateful to Prof. Dr. O. Nuyken for his helpful suggestions with respect to the catalytic reactions and to the International Graduate School of Science and Engineering (IGSSE) for financial support.

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Received: February 24, 2008
Published Online: May 14, 2008

  