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Synthesis, Characterization and Application of Nitrile-Ligated Zinc(II) Complexes Incorporating (Fluoroalkoxy)aluminates

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Nitrile-ligated zinc(II) complexes incorporating aluminum-based weakly coordinating anions (WCAs) have been successfully prepared and fully characterized. An X-ray crystal structure proves both the octahedral symmetry of the zinc(II) cation having six nitrile ligands and the non-coordinating nature of the anion. Similar to complexes bearing boran-based WCAs, the compounds described here can be applied to polymerize isobutylene at room temperature resulting in polyisobutylene with a high content of *exo* double bonds.

Introduction

Transition metal cations or complexes stabilized by neutral, nonaqueous mono- or bidentate ligands are important in numerous synthetic processes.[1] Among the most promising of such compounds for applications both in synthesis and in catalysis are those incorporating easily dissociable solvent ligands, with the nitrile-ligated complexes being one of the longest known and best studied.[2]

Our group has been working on synthesis of acetonitrile/benzonitrile-ligated transition metal complexes[3] and their catalytic applications in organic transformations.[4] Acetonitrile-ligated manganese(II) complexes of the formula $[Mn(NCCH_3)_6][A]_2$ (A = $[B(C_6F_5)_4]^-$, $[B(C_6H_3(CF_3)_2)_4]^-$, and $[(C_6F_5)_3BC_3H_3N_2B(C_6F_5)_3]^-$) are able to initiate the polymerization of isobutylene at room temperature, affording highly reactive polyisobutylenes (HR-PIB) with high content of *exo* double bonds.[5] Similar copper(II)[6] and molybdenum(III) congeners,[7] as well as other first row transition metals[8] were also proven to have similar or even higher activities.

Very recently, we reported on the synthesis of nitrile-ligated silver(I) and copper(II) complexes with (per/polyfluoroalkoxy)aluminates as counteranions: $[Ag(NCCH_3)_4][Al(OC(CF_3)_3)_4]$[9] and $[Cu(NCR')_6][Al(OC(CF_3)_2R)_4]_2$ (R′ = CH_3, Ph; R = CF_3, Ph, $PhCH_3$).[10] The very good activities of copper(II) complexes for olefin aziridination[10,11] demonstrated the superiority of (per/polyfluoroalkoxy)-aluminates (Figure 1) in comparison to other classical WCAs as counteranions for this type of complexes. First reported in 2001,[12] $[Al(OC(CF_3)_3)_4]^-$ has been applied as counteranion for $[H(OEt_2)_2]^+$[13] and $[AlCp_2]^+$[14] for the polymerization of isobutylene. In this work, the synthesis and characterization of acetonitrile and benzonitrile-ligated zinc(II) complexes $[Zn(NCR')_6][Al(OC(CF_3)_2R)_4]_2$ (R′ = CH_3, Ph; R = CF_3, Ph, $PhCH_3$) and first results concerning their catalytic application in room temperature polymerization of isobutylene are presented.

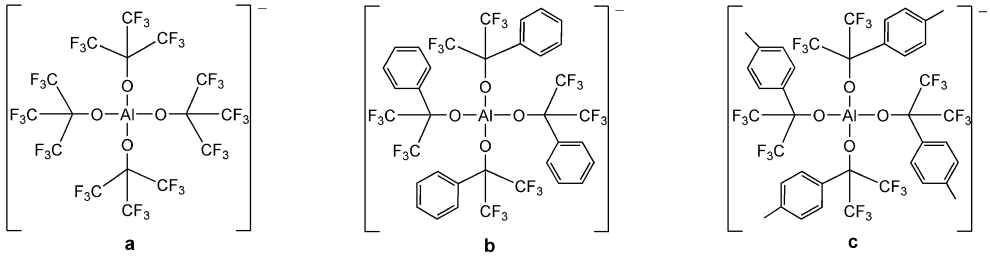

Figure 1. Poly/perfluorinated aluminates WCAs **a**–**c**.

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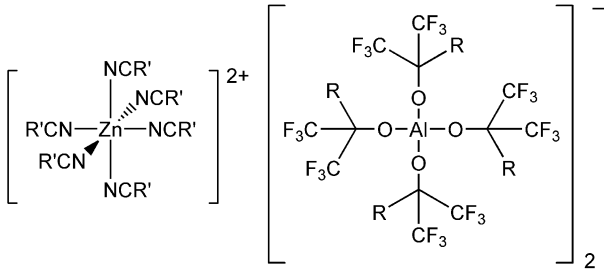
Results and Discussion

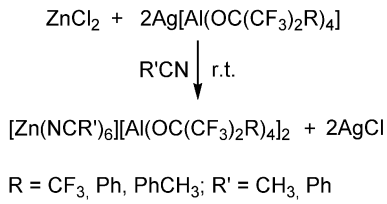
Synthesis and Characterization

Zinc(II) complexes **1**–**6** (Figure 2) are synthesized by reacting zinc(II) chloride with silver salts of the corresponding anions in acetonitrile or benzonitrile (Scheme 1). Complexes **1**–**6** are air- and moisture-sensitive and need to be stored under argon atmosphere at low temperature (–30 °C).



1: R = CF_3, R' = CH_3; **2**: R = CF_3, R' = Ph; **3**: R = Ph, R' = CH_3; **4**: R = Ph, R' = Ph; **5**: R = $PhCH_3$, R' = CH_3; **6**: R= $PhCH_3$, R' = Ph

Figure 2. Structures of complexes **1**–**6**.



Scheme 1. Synthesis of zinc(II) complexes **1**–**6**.

Unlike their copper(II) congeners, complexes **1**–**6** are diamagnetic and therefore suitable for NMR measurements. All spectra (^1H, ^{13}C, ^{19}F, ^{27}Al) are in good agreement with expected and reported values.[12,15] ^{19}F NMR spectra show that the substitution of CF_3 by Ph or $PhCH_3$ in complexes **3**–**6** causes a shift of the singlet signal to ca, –74.6 ppm, which is slightly higher than the value of –75.55 and –75.43 ppm in complexes **1** and **2**, respectively, indicating the electron-donating property of Ph and $PhCH_3$ substituents. The chemical shifts of the aluminum atoms in ^{27}Al NMR spectra are found in the range of 30–34 ppm, and can be assigned to tetracoordinated (per/polyfluoroalkoxy)aluminates.[12]

The FT-IR spectra of complexes **1**–**6** exhibit two sharp ν_{CN} absorptions of medium intensity for acetonitrile-ligated compounds and only one peak for the benzonitrile congeners (Table 1). It is noteworthy that the ν_{CN} absorptions are almost identical for acetonitrile-ligated complexes **1**, **3** and **5**, as well as for benzonitrile-ligated complexes **2**, **4** and **6**, respectively. This observation suggests that changing counteranions from **a** to **b** or **c** has little influence on the coordination environment of the zinc(II) cation in solid state, and might be considered as an indirect proof that anion **b** and **c** are as weakly coordinating as the perfluorinated anion **a**. The higher energies of all ν_{CN} absorptions in comparison to free acetonitrile is caused by σ donation of electron density from the lone pair of the nitrogen to the metal center.[16] The presence of two ν_{CN} absorptions in complexes **1**, **3**, **5** is consistent with octahedral coordination of the metal center. The presence of only one absorption for the benzonitrile compounds can be attribute to a reduced symmetry of the structure with respect to the acetonitrile complexes.

Table 1. FT-IR vibrational frequencies ν_{CN} from **1**–**6**.

Complex	**1**	**2**	**3**	**4**	**5**	**6**
ν_{CN} [cm^{-1}]	2322, 2296	2269	2321, 2293	2262	2321, 2294	2266

The X-ray crystal structure of complex **5** (Figure 3) proves the octahedral symmetry of the zinc(II) cation and the non-coordinating nature of the anion. However, due to severe disorders in the anionic fragment, a detailed discussion concerning the bond lengths and angles appears not to be appropriate.

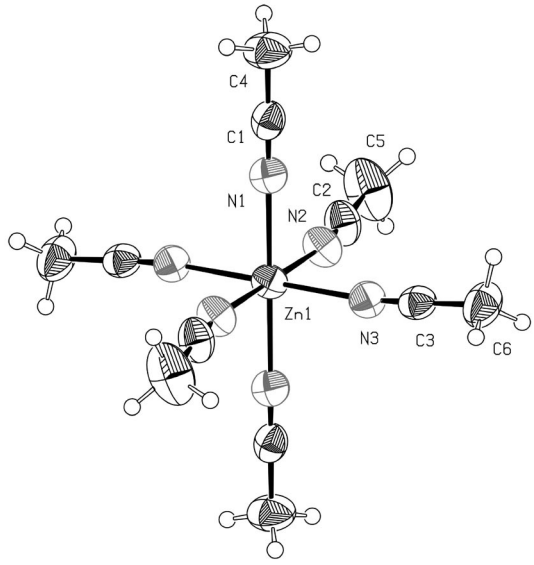


Figure 3. ORTEP style plot of the cationic part of compound **5** in the solid state.[17] Thermal ellipsoids are drawn at the 50% probability level.

Polymerization of Isobutylene

The zinc(II) complex **2** was exemplary tested for the polymerization of isobutylene according to earlier described procedures.[5b,6b] Excellent yield of polyisobutylene (99%) is obtained at room temperature (30 °C) with complex **2** after 20 h reaction time (entry 1, Table 2). Reducing the initiator loading from 5.0×10^{-4} mol L^{-1} to 1.25×10^{-4} mol L^{-1} provide a similar result, with only insignificantly lower yield (93%). Further investigation show that a yield as high as 87% can be achieved only after one hour reaction time (entry 3, Table 2), with an *exo* double bond content of 72% as calculated from the earlier reported various unsaturated double bonds isomers detected.[5c]

Table 2. Polymerization of isobutylene with complex **2** as initiator.[a]

Cat. concentration [mol L^{-1}]	Reaction time [h]	Conversion [%]	Mn [g mol^{-1}]	PDI
5.0×10^{-4}	20	99	1700	3.2
1.25×10^{-4}	20	93	1850	3.5
0.5×10^{-4}	1	87	1500	2.7

[a] Initiator: complex **2**; T = 30 °C; solvent: CH_2Cl_2; c_{IB} = 1.78 mol L^{-1}.

The results shown in Table 2 are comparable to those of earlier described systems, incorporating tetrakis(pentafluorophenyl)borate as counteranion,[8] showing complex **2** is also a very effective initiator for polymerization of isobutylene at room temperature.

Conclusions

Zinc(II) complexes incorporating poly/perfluorinated aluminates as counteranions were synthesized and fully characterized. They are easily synthesized and accessible in good yields. Concerning potential applications, preliminary results show that complex **2** is an active initiator for isobutylene polymerization as its tetrakis(pentafluorophenyl)-borate congener. Further work on testing other complexes as initiators for isobutylene polymerization and the investigation of counteranion effect is currently under way in our laboratories.

Experimental Section

General Procedure for the Synthesis of $[Zn(NCCH_3)_6][Al(OC(CF_3)_2R)_4]_2$ (R = CF_3, Ph, $PhCH_3$): $ZnCl_2$ (0.95–1.1 equiv.) was added to an acetonitrile solution (10 mL) of $[Ag(CH_3CN)_n][Al(OC(CF_3)_2R)_4]$ (2.0 equiv.) (n = 2, 4; R = CF_3, Ph, $PhCH_3$). The resulting mixture was stirred for 3 h with exclusion of light. After filtration, the volatiles were removed in vacuo, affording the product as a white solid. For **1**, the crude product was re-dissolved in 1.5 mL of acetonitrile, filtered and layered by 10 mL of dichloromethane to afford purified product; for **3** and **5**, the crude product was re-dissolved in 10 mL of dichloromethane, filtered and the volatiles were removed in vacuo to afford purified products.

$[Zn(NCCH_3)_6][Al(OC(CF_3)_3)_4]_2$ (1): $ZnCl_2$ (0.036 g, 0.26 mmol), $[Ag(CH_3CN)_4][Al(OC(CF_3)_3)_4]$ (0.62 g, 0.5 mmol); yield 0.60 g (93%). $C_{44}H_{18}Al_2F_{72}N_6O_8Zn$ (2245.91): calcd. C 23.52, H 0.80, N 3.74, F 60.91; found C 23.64, H 0.79, N 3.62, F 60.27. ^{1}H NMR (400 MHz, CD_3CN, 25 °C): δ = 1.95 (s) ppm. ^{13}C NMR (101 MHz, CD_3CN, 25 °C): δ = 126.74, 123.82, 120.93, 118.37, 117.59 ppm. ^{19}F NMR (376 MHz, CD_3CN, 25 °C): δ = –75.55 ppm. ^{27}Al NMR (104 MHz, CD_3CN, 25 °C): δ = 34.04 ppm. IR (Nujol; selected data): $\tilde{\nu}$ = (CN) 2322, 2296 cm^{-1}.

$[Zn(NCCH_3)_6][Al(OC(CF_3)_2Ph)_4]_2$ (3): $ZnCl_2$ (0.033 g, 0.24 mmol), $[Ag(NCCH_3)_2][Al(OC(CF_3)_2Ph)_4]$ (0.6 g, 0.5 mmol); yield 0.49 g (88%). $C_{84}H_{58}Al_2F_{48}N_6O_8Zn$ (2310.69): calcd. C 43.66, H 2.53, N 3.69, F 39.47; found C 43.24, H 2.79, N 3.32, F 39.02. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 7.78 (d, J = 7.9 Hz, 16 H), 7.72 (t, J = 7.5 Hz, 6 H), 7.67 (d, J = 7.8 Hz, 12 H), 7.24 (t, J = 7.3 Hz, 8 H), 7.10 (t, J = 7.8 Hz, 16 H), 2.07 (s, 18 H) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2, 25 °C): δ = 135.10, 128.63, 128.34, 127.92, 127.52, 125.46, 122.56, 119.65, 118.01 ppm. ^{19}F NMR (376 MHz, CD_2Cl_2, 25 °C): δ = –74.61 ppm. ^{27}Al NMR (104 MHz, CD_2Cl_2, 25 °C): δ = 33.78 ppm. IR (Nujol; selected data): $\tilde{\nu}$ = (CN) 2321, 2293 cm^{-1}.

$[Zn(NCCH_3)_6][Al(OC(CF_3)_2PhCH_3)_4]_2$ (5): $ZnCl_2$ (0.033 g, 0.24 mmol), $[Ag(NCCH_3)_2][Al(OC(CF_3)_2PhCH_3)_4]$ (0.62 g, 0.5 mmol); yield 0.45 g (85%). $C_{92}H_{74}Al_2F_{48}N_6O_8Zn$ (2422.90): calcd. C 45.61, H 3.08, N 3.47, F 37.64; found C 45.50, H 3.16, N 3.29, F 37.00. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 7.68 (d, J = 8.2 Hz, 16 H), 6.97 (d, J = 8.2 Hz, 16 H), 2.29 (s, 24 H), 2.04 (s, 18 H) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2, 25 °C): δ = 138.46, 132.18, 128.43, 128.22, 127.86, 125.54, 122.64, 119.75, 20.70, 1.31 ppm. ^{19}F NMR (376 MHz, CD_2Cl_2, 25 °C): δ = –74.67 ppm. ^{27}Al NMR (104 MHz, CD_2Cl_2, 25 °C): δ = 33.56 ppm. IR (Nujol; selected data): $\tilde{\nu}$ = (CN) 2321, 2294 cm^{-1}.

General Procedure for the Synthesis of $[Zn(NCC_6H_5)_6][Al(OC(CF_3)_3)_4]_2$ (2), $[Zn(NCC_6H_5)_6][Al(OC(CF_3)_2Ph)_4]_2$ (4) and $[Zn(NCC_6H_5)_6][Al(OC(CF_3)_2PhCH_3)_4]_2$ (6): $ZnCl_2$ (1.1 equiv.) was added to a benzonitrile solution (4 mL) of $[Ag(CH_3CN)_n][Al(OC(CF_3)_2R)_4]$ (2.0 equiv.) (n = 2, 4; R = CF_3, Ph, $PhCH_3$). The resulting mixture was stirred for 8 h under exclusion of light. After filtration the volatiles were removed in vacuo to afford the product as a white solid, which was re-dissolved in 10 mL of dichloromethane, filtered and the volatiles were removed in vacuo to afford the pure product.

$[Zn(NCC_6H_5)_6][Al(OC(CF_3)_3)_4]_2$ (2): $ZnCl_2$ (0.033 g, 0.24 mmol), $[Ag(CH_3CN)_4][Al(OC(CF_3)_3)_4]$ (0.62 g, 0.5 mmol); yield 0.58 g (90%). $C_{74}H_{30}Al_2F_{72}N_6O_8Zn$ (2618.32): calcd. C 33.95, H 1.15, N 3.21, F 52.24; found C 33.64, H 1.46, N 3.17, F 51.87. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C,): δ = 7.74 (m, 18 H), 7.54 (m, 12 H) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2, 25 °C): δ = 135.82, 133.15, 129.80, 125.52, 122.62, 119.70, 119.09, 116.80, 107.61 ppm. ^{19}F NMR (376 MHz, CD_2Cl_2, 25 °C): δ = –75.43 ppm. ^{27}Al NMR (104 MHz, CD_2Cl_2, 25 °C): δ = 33.56 ppm. IR (Nujol; selected data): $\tilde{\nu}$ = (CN) 2269 cm^{-1}.

$[Zn(NCC_6H_5)_6][Al(OC(CF_3)_2Ph)_4]_2$ (4): $ZnCl_2$ (0.033 g, 0.24 mmol), $[Ag(NCCH_3)_2][Al(OC(CF_3)_2Ph)_4]$ (0.6 g, 0.5 mmol); yield 0.55 g (85%). $C_{114}H_{70}Al_2F_{48}N_6O_8Zn$ (2683.11): calcd. C 51.03, H 2.63, N 3.13, F 33.99; found C 50.36, H 3.09, N 3.05, F 33.50. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 7.70 (d, J = 7.9 Hz, 16 H), 7.64 (t, J = 7.5 Hz, 6 H), 7.58 (d, J = 7.8 Hz, 12 H), 7.41 (t, J = 7.8 Hz, 12 H), 7.16 (t, J = 7.3 Hz, 8 H) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2, 25 °C): δ = 136.04, 135.57, 133.30, 129.95, 128.40, 128.34, 127.98, 127.36, 125.44, 122.54, 119.58, 107.40, 53.46 ppm. ^{19}F NMR (376 MHz, CD_2Cl_2, 25 °C): δ = –74.58 ppm. ^{27}Al NMR (104 MHz, CD_2Cl_2, 25 °C): δ = 30.35 ppm. IR (Nujol; selected data): $\tilde{\nu}$ = (CN) 2262 cm^{-1}.

$[Zn(NCC_6H_5)_6][Al(OC(CF_3)_2PhCH_3)_4]_2$ (6): $ZnCl_2$ (0.033 g, 0.24 mmol), $[Ag(NCCH_3)_2][Al(OC(CF_3)_2PhCH_3)_4]$ (0.62 g, 0.5 mmol); yield 0.55 g (82%). $C_{122}H_{86}Al_2CuF_{48}N_6O_8$ (2793.46): calcd. C 52.42, H 3.10, N 3.01, F 32.62; found C 51.70, H 2.99, N 2.92, F 32.70. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 7.82 (m, 18 H), 7.67 (d, J = 8.1 Hz, 16 H), 7.55 (t, J = 8.0 Hz, 12 H), 6.94 (d, J = 8.1 Hz, 16 H), 2.27 (s, 24 H) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2, 25 °C): δ = 138.25, 136.84, 133.76, 132.30, 130.07, 128.38, 128.11, 127.79, 125.49, 122.59, 120.86, 119.69, 105.99, 20.74 ppm. ^{19}F NMR (376 MHz, CD_2Cl_2, 25 °C): δ = –74.64 ppm. ^{27}Al NMR (104 MHz, CD_2Cl_2, 25 °C): δ = 32.48 ppm. IR (Nujol; selected data): $\tilde{\nu}$ = (CN) 2266 cm^{-1}.

X-ray Structure Determination on Complex 5: Data collection was aborted because of the highly disordered anionic part. Colorless

fragment, monoclinic, space group $P2_1/c$ (No. 14), a = 25.0008(6), b = 20.3629(5), c = 22.9063(5) Å, β = 112.6256(12)°, V = 10763.9(4) Å^3, Z = 4. Preliminary examination and data collection were carried out on Kappa APEX II (Area Diffraction System; Bruker AXS) with an Oxford Cryostream cooling system at the window of a rotating anode with graphite-monochromated Mo-K_α radiation. Data collection was performed at 153 K.

Polymerization of Isobutylene: For determination of the activity of complex **2**, the polymerization reactions were carried out in pressure tubes in a glove box. Each tube was filled with (over molecular sieves) dichloromethane (20 mL) and the pre-calculated amounts of catalyst and are being kept cooled constantly at –25 °C before the addition of the monomer. A pre-condensed amount of isobutylene is then added and the pressure tube is sealed and removed from the glove box. The polymerization was preformed in a water bath, the temperature of which was maintained at 30 °C. The polymerization was quenched by adding methanol (5 mL). The product obtained was passed through alumina to remove traces of the complexes. The solvent was removed in vacuo to afford the purified product. The *exo* double bond content was determined by ^{1}H NMR (Bruker Avance 400 spectrometer operating at 500.13 MHz for ^{1}H NMR, solvent $CDCl_3$) and molecular weight via GPC (Agilent Technologies series 1100 with RI detector; column: Lichrogel PS 40; solvent: chloroform; polystyrene calibration).

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[17] a) Single-crystal X-ray structure determination of compound **5**: $C_{92}H_{74}Al_2F_{48}N_6O_8Zn$, M_r = 2422.93, monoclinic, space group $P2_1/c$ (no. 14), a = 25.0008(6), b = 20.3629(5), c = 22.9063(5) Å, β = 112.6256(12), V = 10763.9(4) Å^3, T = 153 K, Z = 4, D_c = 1.495 g cm^{-3}, μ(Mo-K_α) = 0.382 mm^{-1}. After merging of 180830 reflections (R_{int} = 0.029) a sum of 11248 (all data) and 10474 [$I_o > 2\sigma(I_o)$], remained. The refinements were stopped due to severe disorder in the anionic part of compound **5** at $R1$ = 0.0681 [$I_o > 2\sigma(I_o)$], $wR2$ = 0.1769 (all data), and GOF = 1.219; b) APEX suite of crystallographic software: *APEX 2*, v. 2008.4, Bruker AXS Inc., Madison, Wisconsin, USA, **2008**; c) *SAINT*, v. 7.56a and *SADABS*, v. 2008/1, Bruker AXS Inc., Madison, Wisconsin, USA, **2008** ; d) , *WinGX* (v. 1.70.01, January **2005**): L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

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