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Synthetic and Structural Investigations on the Reactivity of the Cd−I Bond in [ICd{$Zr_2(OPr^i)_9$}] to Construct New Mixed-Metal Alkoxides

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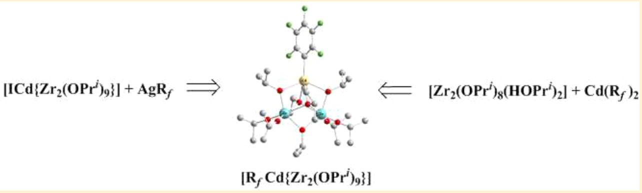
Supporting Information

ABSTRACT: New mixed-metal alkoxides of general formula [XCd{$Zr_2(OPr^i)_9$}]$_n$ (X = $-C_2F_5$, $-C_6F_5$, $-C_6F_4$-4-H, $-NO_3$, −NCO, $-SO_3CF_3$, $-O_2CCF_3$, $-O_2CC_2F_5$, $-O_2CCH_3$, $-ClO_4$, −CN, $-SO_4$; n = 1, 2) were obtained by the scission of the Cd−I bond in the iodo heterobimetallic isopropoxide [ICd{$Zr_2(OPr^i)_9$}] (**1**), whereby the underlying synthetic strategies involve metathesis reactions with silver salts or Lewis acid−base interactions between the Brønsted acid [$Zr(OPr^i)_4(HOPr^i)$]$_2$ and bis(fluoroorgano)cadmium ($Cd(R_f)_2$) compounds. The new compounds were characterized by multinuclear NMR spectroscopy, elemental analysis, and mass spectrometry. The results of X-ray diffraction analysis of [(F_5C_6)Cd{$Zr_2(OPr^i)_9$}] (**2**), [(4-H-F_4C_6)Cd{$Zr_2(OPr^i)_9$}] (**3**), [(F_5C_2)Cd{$Zr_2(OPr^i)_9$}]$_2$ (**4**), [(ONO_2)Cd{$Zr_2(OPr^i)_9$}]$_2$ (**5**), [(CH_3CO_2)Cd{$Zr_2(OPr^i)_9$}] (**6**), [(O_2ClO_2)(H_5C_3N)Cd{$Zr_2(OPr^i)_9$}] (**7**), [(μ-O_2ClO_2)Cd{$Zr_2(OPr^i)_9$}]$_2$ (**8**), [(μ-O_2CCF_3)-Cd{$Zr_2(OPr^i)_8(O_2CCF_3)$}]$_2$ (**9**), [(μ-$O_2CC_2F_5$)Cd{$Zr_2(OPr^i)_8(O_2CC_2F_5)$}]$_2$ (**10**), [(μ(*O*,*N*)-OCN)Cd{$Zr_2(OPr^i)_9$}]$_2$ (**11**), and [(μ-O_2SOCF_3)Cd{$Zr_2(OPr^i)_9$}]$_2$ (**12**) revealed the molecular framework to be formally constituted by tetradentate coordination of a nonaisopropoxo dizirconate unit, {$Zr_2(OPr^i)_9$}$^-$, to a CdX^+ unit. In solution and in the solid state, **1**−**7** exist as monomers, whereas compounds **8**−**12** form dimers.



INTRODUCTION

The chemistry of M−O−C derivatives represents a cutting edge frontier of chemical research, especially due to the increasing importance of molecular heterometallic systems as potential precursors enabling phase-selective synthesis of multimetallic oxide materials by atomic scale mixing of cations.[1] A large number of heterometallic alkoxides which can be used as single-source precursors for the synthesis of oxide ceramics are known in the literature.[2] In addition to homoleptic ($MM'(OR)_x$), heteroleptic ($MM'(OR)_x(X)_y$ where X = OAc, OR′, halide), and oxo alkoxide species ($MM'O(OR)_x$ or $MM'(OR)_x(X)_y$), alkoxide derivatives with different metal combinations and up to three different metals[3] in a single molecule show the rich synthetic and structural chemistry of metal alkoxides.[4] However, structural data on heterometallic, fluorinated molecular alkoxides have not been reported so far, which motivated us to investigate the metathesis of the metal−halogen bond in [ICd{$Zr_2(OPr^i)_9$}] (**1**).[3]

The iodocadmium zirconium isopropoxide is an interesting starting material, due to its monomeric nature in the solid state, solution, and gas phases imparted by the strong tetradentate chelation of the {$Zr_2(OPr^i)_9$} unit (Figure 1) that endows stability to the triangular "$CdZr_2$" framework, making **1**[3] a viable synthon to construct new bi- and trimetallic alkoxide derivatives by the metathesis of the Cd−I bond.

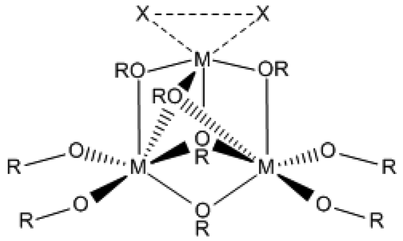


Figure 1. Tetradentate coordination mode of {$M_2(OR)_9$}$^-$ units in heterometallic alkoxides.[5]

In comparison to the large number of homometallic mixed-ligand compounds,[6] structurally characterized examples of heterometallic heteroleptic derivatives with fluorinated ligands or weakly coordinating anions (WCA) have been less investigated. In this work, a series of alkoxide derivatives of the type [XCd{$Zr_2(OPr^i)_9$}], where X represents fluorinated or other ligands, were synthesized as synthons to construct novel heterotrimetallic alkoxides or to obtain new heterobimetallic systems as possible precursors to metal oxides or oxyfluorides.

RESULTS AND DISCUSSION

Heterobimetallic derivatives of the general formula [XCd{$Zr_2(OPr^i)_9$}] were accessible by salt elimination and Lewis acid−base condensation reactions, as depicted in Scheme 1.

Reactions of 1[3] with Silver Compounds. The reactions between trimethylperfluoroorganosilanes and silver(I) fluoride offered a convenient access to perfluoroorganosilver(I)

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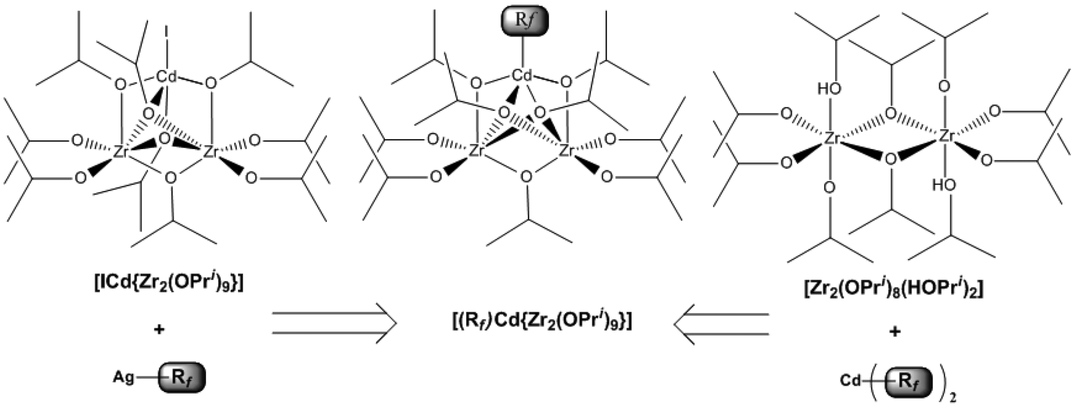
Scheme 1. Synthetic Routes to Complexes 2−14



compounds, as reported for reactions with the trifluoromethyl and pentafluorophenyl groups in propionitrile and other N-donor solvents.[7]

In order to elucidate the chemical nature of Cd−I bonds, **1**[3] was reacted with various silver derivatives (AgC_6F_5, AgC_6F_4-4-H, $AgNO_3$, $AgSO_3CF_3$, AgO_2CCF_3, $AgO_2CC_2F_5$, AgC_2F_5, AgO_2CCH_3, AgCN, $AgClO_4$, Ag_2SO_4, and AgOCN) in a mixture of propionitrile, toluene, and heptane by stirring the reaction mixtures at room temperature for 12 h. Given the low propensity of silver to form strong Ag−O bonds and the facile elimination of AgI, reactions are pushed to completion, indicating this approach to be an interesting pathway toward salt-elimination reactions in alkoxide chemistry.

$$[\mathrm{ICd}\{\mathrm{Zr}_2(\mathrm{OPr}^i)_9\}] + \mathrm{AgR} \xrightarrow[-\mathrm{AgI}]{} [\mathrm{RCd}\{\mathrm{Zr}_2(\mathrm{OPr}^i)_9\}]$$

The elimination of silver salts is a more effective strategy, due to the low solubility of AgI in common organic solvents, which makes it a better leaving group than alkali-metal halides or $[NMe_4]$ halides. A survey of some Cd−I bond lengths described in the literature shows the Cd−I bond in **1**[3] (2.637(4) Å) to be one of the shortest in comparison to those in other iodo-cadmium derivatives structurally characterized so far (Table 1), indicating a uniquely strong Cd−I interaction in **1**,[3] which was supported by mass spectrometric data.

Cleavage of Cd−C Bonds by Lewis Acid−Base Interactions. On the basis of earlier reports on the formation of $Cd(C_6F_5)X$[9] by reactions between HX and $Cd(C_6F_5)_2$,[7c] we have studied the reaction between $Cd(C_6F_5)_2$ and $[Zr(OPr^i)_4(HOPr^i)]_2$.[10] For the synthesis of fluoroorgano derivatives of **1**,[3] both salt metathesis with Ag salts and acidic cleavage of cadmium−carbon bonds by $[Zr(OPr^i)_4(HOPr^i)]_2$ were applied to the synthesis of **2** (Scheme 1) in high yields.

$$[\mathrm{Zr}(\mathrm{OPr}^i)_4(\mathrm{HOPr}^i)]_2 + \mathrm{Cd}(\mathrm{R}_f)_2 \xrightarrow[-\mathrm{R}_f\mathrm{H},-\mathrm{HOPr}^i]{} [(\mathrm{R}_f)\mathrm{Cd}\{\mathrm{Zr}_2(\mathrm{OPr}^i)_9\}]$$

In contrast to the reaction of $Cd(C_6F_5)_2$ and $[Zr(OPr^i)_4(HOPr^i)]_2$, which proceeded selectively to form **2**, the $Cd(CF_3)_2$·(glyme) adduct reacted differently to form $[(F_3C)Cd\{Zr_2(OPr^i)_9\}]$ with concomitant formation of HCF_2OPr^i and HF, followed by successive substitution of fluorine for isopropoxy groups at the CF_3 group still bonded to Cd, giving finally a reaction mixture of difluoromethyl isopropyl ether, HCF_2OPr^i, as the minor product and triisopropyl orthoformate, $HC(OPr^i)_3$, as the major product. Both compounds were unambiguously identified by ^1H, ^{13}C, and ^{19}F NMR spectroscopy. It is noteworthy that no spectroscopic evidence was found for the missing link in this process, $CHF(OPr^i)_2$, in either the present investigation or in previous studies.[11] HF produced during the process is consumed by the $[Cd\{Zr_2(OPr^i)_9\}]^-$ framework to plausibly form "$[Cd\{Zr_2(OPr^i)_{9-n}F_n\}]$" or related clusters of indefinite composition and to release $HOPr^i$.

Table 1. I−Cd Bond Lengths in Known Cd Compounds or Ions[3,8]

	Cd−I bond, Å
$[ICd\{Zr_2(OPr^i)_9\}]$ (**1**)	2.637(4)
$\sum$ cov radii	2.83
$\sum$ ion radii	3.03
$[CdI_3]^-$	2.708(1), 2.717(1), 2.741(1)

Multinuclear NMR Analysis. The assignment of the isopropoxy groups in **1**−**14** (Table 2) was achieved using a combination of 1D and 2D (^1H,^1H-COSY, ^1H,^{13}C-HSQC, ^1H,^{13}C-HMBC, ^1H,^1H-NOESY) NMR experiments. The ^{113}Cd signals were detected either by direct methods or by inverse ^1H,^{113}Cd-HMQC experiments optimized for 40 Hz. In particular, ^{113}Cd NMR acts as a sensitive probe for monitoring the changes in cadmium coordination sphere[12] and the nature of the ligands.[13] The chemical shifts of ^{113}Cd NMR as a function of the nature of the ligands are plotted in Scheme 2.

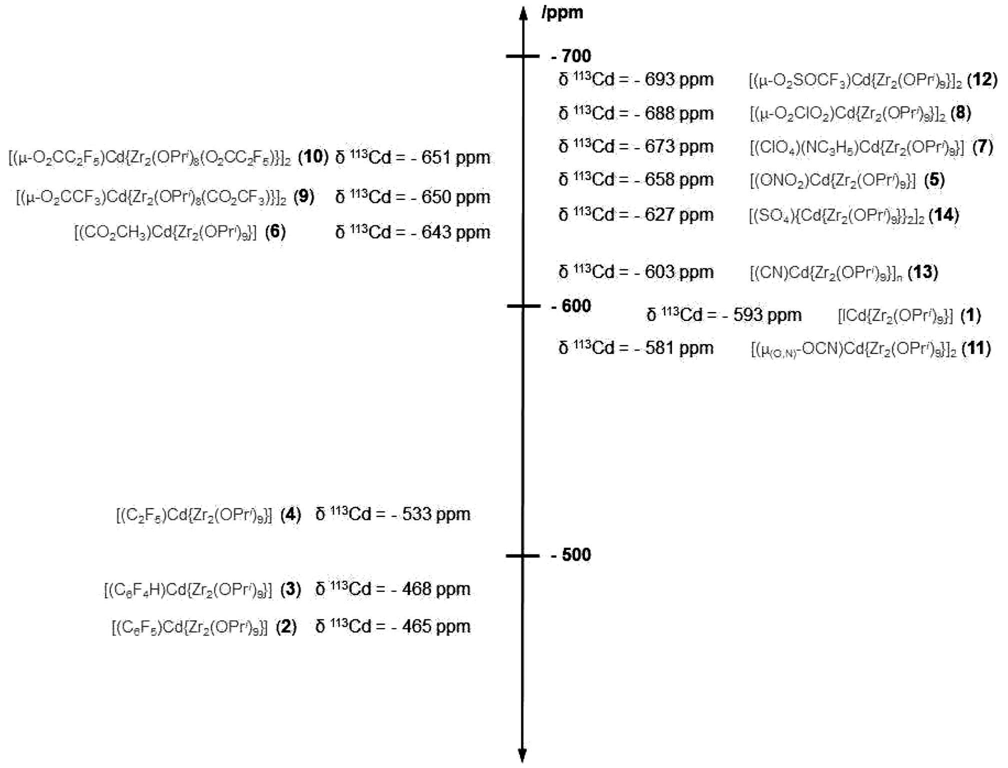
While compounds **1**, **2**, **5**−**10**, **12**, and **14** displayed a rigid behavior in solution at ambient temperature, allowing the assignment of the terminal as well as bridging OPr^i groups on Zr, the doubly bridged (μ_2-Zr_2) OPr^i groups, and the μ_2 OPr^i (Cd−Zr) and μ_3 OPr^i (Cd−Zr_2) units, compounds **3**, **4**, **11**, and **13** displayed a fluxional behavior, which prevented a distinct assignment of all signals even at low temperatures (down to −70 °C).

In comparison to the deceptively simple spectroscopic pattern generally observed for fluxional alkoxide molecules,[14] as seen for the derivatives **3**, **4**, **11**, and **13**, the ^1H and ^{13}C NMR spectra of other derivatives are indicative of a rigid structural pattern existing in solution.[3,15] For instance, the room-temperature ^1H NMR spectra of **2** in toluene-d_8 showed four doublets for the methyl groups in an integrative ratio of 2:1:4:2 corresponding to the nine OPr^i groups, in the region of 1.66−1.21 ppm. The signals of the methine protons were

Table 2. ^1H NMR Chemical Shifts and Assignment (Figure 2) for All Compounds

	terminal Zr−CH/ integrative ratio	μ_2-Zr_2−CH/ integrative ratio	μ_2-CdZr−CH and μ_3-Zr_2Cd−CH/ integrative ratio	terminal Zr−CH_3/ integrative ratio	μ_2-Zr_2−CH_3/ integrative ratio	μ_2-CdZr−CH_3 and μ_3-Zr_2Cd−CH_3/ integrative ratio
1	4.46/4	4.55/1	4.68 and 4.86/2 and 2	1.37/24	1.45/6	1.59 and 1.66/12 and 12
2	4.41/6	4.52/1	(4.41) and 4.59/2	1.37/24	1.42/6	1.21 and 1.66/12 and 12
3	4.52/5		4.69 and 4.77/4	1.40/30		1.61 and 1.77/24
4	4.56/~7		4.69/~2	1.45/~24		1.46/~30
5	4.43/4	4.47/1	4.59 and 4.63/4	1.34/12	1.4/18	1.59 and 1.41/24
6	4.51/4	4.55/1	4.7 and 4.72/4	1.38/24	1.48/6	1.53 and 1.75/24
7	4.5/4	4.5/1	4.6/2 4.7/2	1.4/30		1.7 and 1.6/12 and 12
8	4.41/4	4.5/1	4.6/2 4.7/2	1.32/24	1.4/6	1.56 and 1.6/12 and 12
9	4.34 and 4.44/5		4.55/4	1.28/24	1.36/18	1.57/12
10	4.45 and 4.49/5		4.59 and 4.66/4	1.35/24 1.41/6 1.32/~36		1.39 and 1.64/24
11	4.41/~6		4.55/~3			1.55/~18
12	4.42/4	4.45/1	4.57 and 4.67/4	1.3/24	1.36/6	1.52 and 1.67/12 and 12
13	4.59 and 4.64/5		4.69 and 4.8/4	1.42 and 1.64/30		1.9 and 1.7/24
14	4.49/4	4.58 and 4.73/3	4.88/2	1.38/24	1.45/6	1.77 and 1.73/24

Scheme 2. ^{113}Cd NMR Shifts of Compounds 1−14



observed as three multiplets centered at δ 4.59, 4.52, and 4.41 ppm with the integrative ratio 2:1:6; the last signal results from an overlapping of two septets, as elucidated by 2D NMR experiments. As found in the ambient- and variable-temperature NMR studies of derivatives $[ICd\{M_2(OPr^i)_9\}]$ (M = Sn, Ti, Zr, Hf)[3,15a] and other related complexes,[5a,15b] the observed spectroscopic pattern and the trend of chemical shifts vs connectivities of the isopropoxy groups is a peculiar feature of complexes based on a tetradentate $\{M_2(OPr^i)_9\}^-$ unit.[15c] The number and relative total intensities of the spectroscopic patterns of **2**, **5**−**10**, **12**, and **14** were comparable with those of **1**,[3] and in all cases the spectroscopic pattern could be interpreted in a tetradentate coordination mode for cadmium (see Table 2 and the Supporting Information). The ^{13}C NMR spectral data for all derivatives were consistent with the type of group(s) attached to the metal centers.

The coordination of the fluorinated ligand was elucidated by $^1H,^{19}F$-HOESY NMR experiments as shown in Figure 2 for compound **2**.

For compounds **9** and **10** the solution NMR spectroscopic data are similar and are not in line with the solid-state structures. They exhibited four multiplets in the region 4.66−

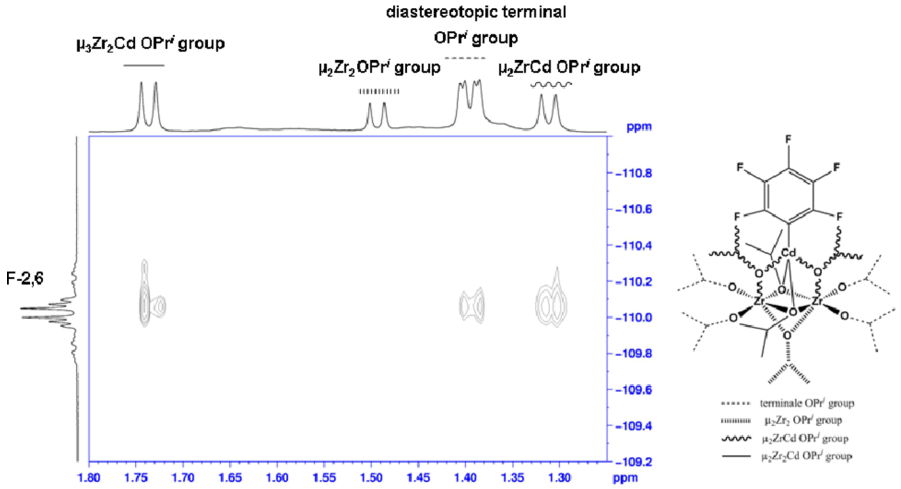


Figure 2. ^{1}H−^{19}F-HOESY NMR spectrum of **2** (room temperature, benzene-d_6).

4.34 ppm, whereby the methine protons of terminal and bridging OPr^i groups showed overlapping resonances. Similar observations were made for the methyl protons in the region 1.64−1.28 ppm. The broad resonances in ^{19}F NMR spectra indicate oligomeric structures and a dynamic behavior in solution, as shown in Figure 3.

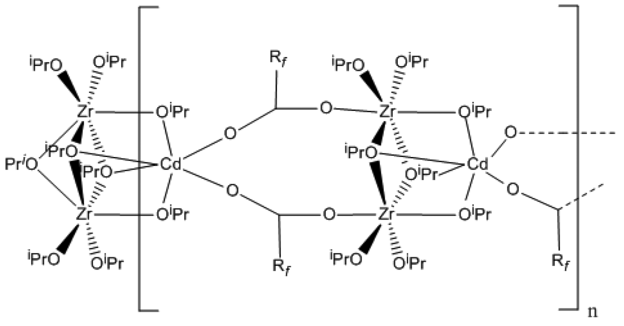


Figure 3. Proposed structure in solution for **9** and **10** (R_f = $-O_2CCF_3$, $-O_2CC_2F_5$).

In contrast to the stereochemically rigid [ICd{Zr$_2$(OPr^i)$_9$}] (**1**),[3] the ^{1}H and ^{13}C NMR spectra of [(F$_5$C$_2$)Cd{Zr$_2$(OPr^i)$_9$}] (**4**), [(μ(*O*,*N*)-OCN)Cd{Zr$_2$(OPr^i)$_9$}]$_2$ (**11**), [(NC)-CdZr$_2$(OPr^i)$_9$]$_n$ (**13**), and [(4-H-F$_4$C$_6$)Cd{Zr$_2$(OPr^i)$_9$}] (**3**) at 20 °C are deceptively simple, indicating a rapid alkoxide site exchange in solution. The fluxional behavior decelerated upon lowering the temperature, but even −70 °C did not suffice to completely freeze the motion of ligands in compounds **3**, **4**, **11**, and **13**. However, the observed solution ^{113}Cd NMR chemical shifts as well as the pattern of the ^{1}H NMR spectra closely resemble those observed for [ICd{Zr$_2$(OPr^i)$_9$}] (**1**),[3] indicating a similar binding mode (tetradentate) of the {Zr$_2$(OPr^i)$_9$}$^-$ unit to Cd in all cases. The fluorine NMR spectra, as well as the proton NMR spectra, of [(4-H-F$_4$C$_6$)Cd{Zr$_2$(OPr^i)$_9$}] (**3**) showed it to be a pyridine adduct, which again supports the proposed fluxional behavior in solution.

Electron Impact Mass Spectrometry. EI mass spectra (20 eV) of compounds **2**−**10** and **12** reveal comparable fragmentation patterns, with [XCd{Zr$_2$(OPr^i)$_8$}]$^+$ being the predominant fragment. This observation further supports the stability of the CdZr$_2$ unit. Further peaks of lower intensities are mostly ions deriving from the decomposition of the {Zr$_2$(OPr^i)$_9$}$^-$ unit.[16] For compounds **11**, **13**, and **14** mostly ions resulting from the {Zr$_2$(OPr^i)$_9$}$^-$ unit[16] were detectable.

TG/DTA Analysis. TG/DTAs were carried out in sealed aluminum cartridges under a N$_2$ atmosphere in order to observe the decomposition without any additional source of oxygen. TGA of complexes **2**−**6**, **9**, and **13** show just one major decomposition step mostly in the range 190−270 °C, indicating a decomposition to the oxide material with about 40−50 wt % residues left at 600 °C, whereby the theoretical residue is about 40 wt %. For compounds **8**, **10**, and **12** a similar residue occurs via a two- or multiple-step decomposition, whereas **7** and **11** decompose with ca. 60 wt % residues left at 600 °C. Given the susceptibility of the new compounds towards atmospheric moisture, a handling error in the TGA analyses needs to be taken into account; also the formation of metal fluorides in F-containing ligands cannot be completely ruled.

X-ray Diffraction Analysis. The crystallographic data of compounds **2**−**12** are summarized in the Supporting Information, as well as illustrations of the molecular structures of **3**−**5**, **8**, and **10**.

Colorless crystals suitable for X-ray diffraction studies were obtained at room temperature from a mixture of dichloromethane and toluene for compound **2**, a benzene solution for compounds **3**, **5**−**8**, and **10**, and a toluene solution at −12 °C for **4**, **9**, **11**, and **12**.

The central core of all molecules comprised a heterometallic CdZr$_2$ triangle capped by two μ_3-OPr^i ligands; cadmium bore different ligand units, whereas each zirconium possessed two terminal isopropoxide ligands. Each side of the trimetallic planar core is bridged by a μ_2-OPr^i group. The local coordination environment around cadmium resembles a distorted trigonal bipyramid, with two oxygen atoms occupying the axial coordination sites. The Zr−O distances within the {Zr$_2$(OPr^i)$_9$}$^-$ unit show the gradual variation (Zr−O (terminal) < Zr−(μ_2-OZr) (doubly bridging, μ_2) < Zr−(μ_3-OZr) (triply bridging, μ_3)) commonly observed in the confacial bioctahedral structures of the lanthanide, actinide, and early-transition-metal alkoxides.[17] The bond lengths of μ_2-OPr^i ligands fall into two classes, depending on whether a Zr−O−Zr or Zr−O−Cd linkage is present. The structurally characterized heterometallic alkoxides based on the {M$_2$(OR)$_9$}$^-$ unit generally show a trend in which the length of the bonding interaction of the alkoxide oxygen of the {M$_2$(OR)$_9$}$^-$ unit to the coordinated metal atom increases with each successive bridging, which is due to the loss of electron density at the alkoxide oxygen.[5b]

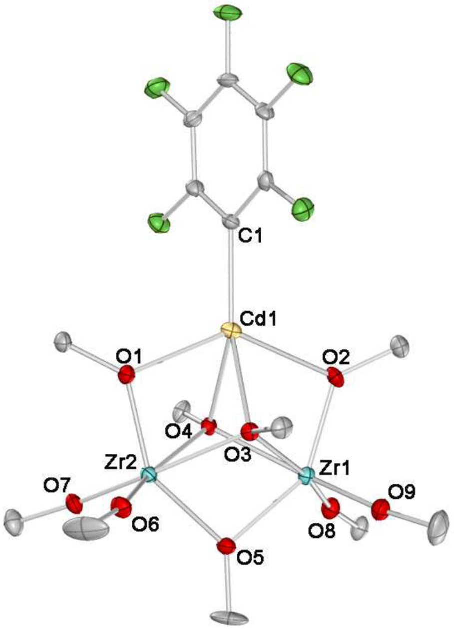


Figure 4. Molecular structure of $[(F_5C_6)Cd\{Zr_2(OPr^i)_9\}]$ (**2**) (100 K). Displacement ellipsoids are drawn at the 30% probability level; methyl carbons and hydrogen atoms of the isopropyl groups are omitted for clarity. Selected lengths (Å) and angles (deg): Cd1−C1 = 2.158(5), Cd1−O1 = 2.352(3), Cd1−O2 = 2.377(3), Cd1−O3 = 2.326(3), Cd1−O4 = 2.330(3), Zr−O = 1.921(3)−2.318(3); O1−Cd1−C1 = 112.12(14), O2−Cd1−C1 = 112.35(14), O3−Cd1−C1 = 151.74(14), O4−Cd1−C1 = 142.64(15), O1−Cd1−O4 = 71.61(10), O2−Cd1−O4 = 71.18(10), O4−Cd1−O3 = 65.63(10), Zr1−O4−Cd1 = 92.78(10), Zr2−O4−Cd1 = 91.36(10).

$[(F_5C_6)Cd\{Zr_2(OPr^i)_9\}]$ (2), $[(4\text{-}H\text{-}F_4C_6)Cd\{Zr_2(OPr^i)_9\}]$ (3), and $[(F_5C_2)Cd\{Zr_2(OPr^i)_9\}]$ (4). Compound **2** (Figure 4) and **3** crystallized isostructurally in the orthorhombic space group *Pbca* (No. 61), whereas compound **4** crystallized in the orthorhombic spacegroup *Pnma* (No. 62). The molecular structures of **2**−**4** closely resemble that of the parent compound $[ICd\{Zr_2(OPr^i)_9\}]$ (**1**)[3] in terms of the binding mode of the $\{M_2(OR)_9\}^-$ unit to the central metal Cd^{II} in a similar tetradentate manner.

As indicated by the multinuclear NMR studies, **2**−**4** exist in the solid state as monomers where the cadmium atom bears a terminal fluorophenyl/fluoroethyl unit and a $\{Zr_2(OPr^i)_9\}^-$ unit binding in a 4-fold fashion via two triply (μ_3) and two doubly (μ_2) bridging isopropoxy groups. The steric bulk of the fluorophenyl groups prevents **2** and **3** from dimerization, and thus they differ from the dimeric complex $[ClCd\{Zr_2(OPr^i)_9\}]_2$ described by Mehrotra et al.[18]

$[(ONO_2)Cd\{Zr_2(OPr^i)_9\}]$ (5) and $[(CH_3CO_2)Cd\{Zr_2(OPr^i)_9\}]$ (6). Compound **5** crystallized in the monoclinic space group $P2_1/n$ with four molecules in the unit cell (Supporting Information). Compound **6** crystallized in the triclinic space group $P\overline{1}$ (No. 2) (Figure 5).

In the solid-state structure of **5**, the NO_3^- group coordinates to cadmium in a bidentate mode with Cd−O contacts of 2.298 Å and a rather acute O−Cd−O angle (55.02°). The N−O bond lengths of 1.235−1.243 Å do not significantly vary from each other. **5** represents the first structurally characterized nitrate heterometal alkoxide derivative based on a $\{M_2(OPr^i)_9\}^-$ unit. Similar to the case for compound **5**, the acetate group in **6** was found to coordinate cadmium in a bidentate mode.

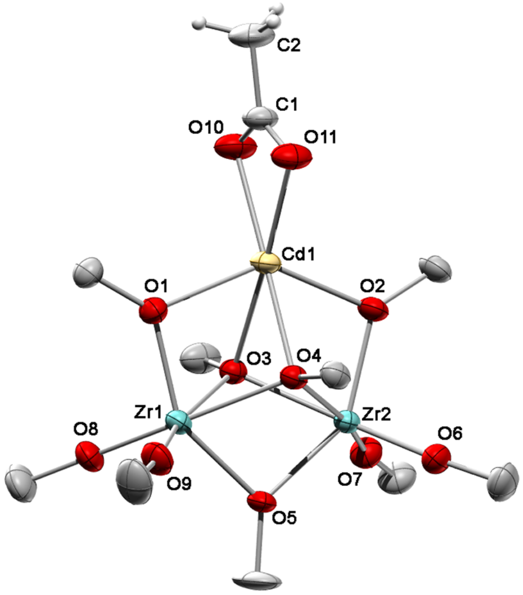


Figure 5. Molecular structure of $[(CH_3CO_2)Cd\{Zr_2(OPr^i)_9\}]$ (**6**) (170 K). The displacement ellipsoids are drawn at the 30% probability level; methyl carbons and hydrogen atoms of the isopropyl groups are omitted for clarity. Selected lengths (Å) and angles (deg): Cd1−O10 = 2.276(3), Cd1−O11 = 2.276(3), Cd1−O1 = 2.319(3), Cd1−O2 = 2.292(3), Cd1−O3 = 2.388(2), Cd1−O4 = 2.360(2), Zr−O = 1.920(3)−2.261(3); O10−Cd1−O11 = 57.25(12), O1−Cd1−O10 = 104.37(13), O2−Cd1−O11 = 110.66(12), O1−Cd1−O11 = 107.58(12), Zr1−O4−Cd1 = 91.27(9), Zr2−O4−Cd1 = 91.17(9).

$[(O_2ClO_2)(H_5C_3N)Cd\{Zr_2(OPr^i)_9\}]$ (7) and $[(\mu\text{-}O_2ClO_2)Cd\{Zr_2(OPr^i)_9\}]_2$ (8). The perchlorate derivative **8** crystallized similarly to **12** (Figure 7) as a dimer bridged by the perchlorate unit in the monoclinic space group $P2_1/c$ (No. 14), whereas the monomeric propionitrile adduct **7** crystallized in the triclinic space group $P\overline{1}$ (No. 2) (Figure 6).

In contrast to the case for compound **8**, dimerization in **7** can be prevented through addition of propionitrile to the reaction mixture so that one propionitrile molecule coordinates to the cadmium atom. The Cd−O contact of the second oxygen atom of the perchlorate group is relatively long with a Cd1−O13 distance of 2.797 Å.

$[(\mu\text{-}O_2SOCF_3)Cd\{Zr_2(OPr^i)_9\}]_2$ (12). Compound **12** crystallized in the monoclinic space group $P2_1/c$ (No. 14) with four molecules in the unit cell (Figure 7). The bond lengths and angles in **12** show only minor differences; in comparison to the pentacoordinated Cd centers in **2**−**4**, the presence of a bridging triflate unit leads to a strongly distorted octahedral configuration around Cd.

$[(\mu_{(O,N)}\text{-}OCN)Cd\{Zr_2(OPr^i)_9\}]_2$ (11). Compound **11** crystallized in the monoclinic space group $P2_1/c$ (no. 14) (Figure 8).

The molecular structure of **11** represents, to the best of our knowledge, the first structurally characterized example of a cyanate-capped bimetallic alkoxide based on a $\{M_2(OPr^i)_9\}^-$ unit. The cyanate unit bridges the two $CdZr_2$ units via an end-to-end coordination, to form the dimeric framework.

$[(\mu\text{-}O_2CCF_3)Cd\{Zr_2(OPr^i)_8(O_2CCF_3)\}]_2$ (9) and $[(\mu\text{-}O_2CC_2F_5)Cd\{Zr_2(OPr^i)_8(O_2CC_2F_5)\}]_2$ (10). In contrast to the case for the nonfluorinated acetate derivative **6**, the solid-state structural

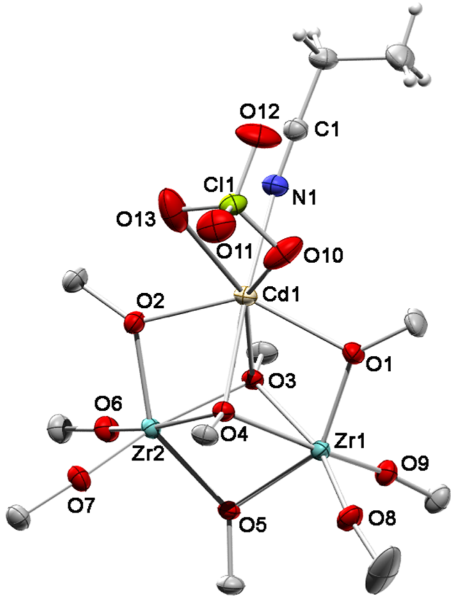


Figure 6. Molecular structure of $[(O_2ClO_2)(H_5C_3N)Cd\{Zr_2(OPr^i)_9\}]$ (**7**) (170 K). The displacement ellipsoids are drawn at the 30% probability level; methyl carbons and hydrogen atoms of the isopropyl groups are omitted for clarity. Selected lengths (Å) and angles (deg): Cd1−N1 = 2.282(2), Cd1−O10 = 2.388(3), Cl1−O10 = 1.436(3), Cl1−O13 = 1.439(3), O2−Cd1 = 2.3017(19), O1−Cd1 = 2.3024(17), O3−Cd1 = 2.4617(17), O4−Cd1 = 2.3024(17), Zr−O = 1.9194(19)−2.3176(17); O2−Cd1−N1 = 109.24(8), O2−Cd1−O10 = 129.82(9), O13−Cl1−O10 = 104.1(2), O1−Cd1−O4 = 73.32(7), O2−Cd1−O = 72.59(6), O4−Cd1−O3 = 64.90(6), Zr1−O4−Cd1 = 92.17(6), Zr2−O4−Cd1 = 93.36(6).

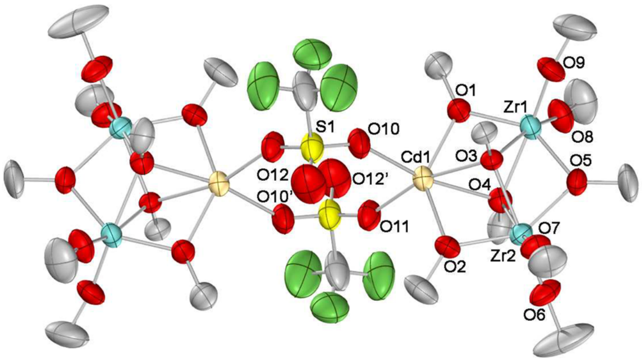


Figure 7. Molecular structure of $[(\mu\text{-}O_2SOCF_3)Cd\{Zr_2(OPr^i)_9\}]_2$ (**12**) (293 K). The displacement ellipsoids are drawn at the 30% probability level; methyl carbons and hydrogen atoms of the isopropyl groups are omitted for clarity. Selected lengths (Å) and angles (deg): Cd1−O10 = 2.256(4), Cd1−O11 = 2.234(5), O11−S1′ = 1.439(4), O10−S1 = 1.433(4), Cd1−O2 = 2.259(4), Cd1−O3 = 2.385(4), Cd1−O4 = 2.410(4), Zr−O = 1.894(5)−2.274(4); O2−Cd1−O10 = 117.26(17), O2−Cd1−O11 = 97.57(17), O3−Cd1−O10 = 104.65(15), O3−Cd1−O11 = 167.87(15), O3−Cd1−O1 = 71.93(14), O3−Cd1−O2 = 72.03(15), Zr1−O3−Cd1 = 91.45(15), Zr2−O3−Cd1 = 90.50(14).

mode of the perfluorinated acetate derivatives **9** (Figure 9) and **10** is changed due to the replacement of the μ_2-Zr_2 isopropoxy group by a perfluorocarboxylate ligand.

The most probable sequence of reactions leading to the formation of such clusters is that one or more alkoxo ligands are replaced by carboxylato ligands in the first step, followed by esterification of the liberated alcohol.

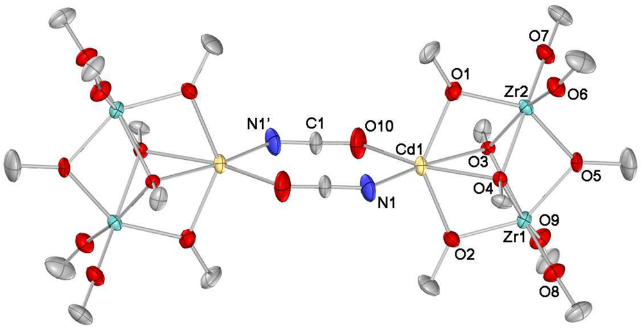


Figure 8. Molecular structure of $[(\mu_{(O,N)}\text{-}OCN)Cd\{Zr_2(OPr^i)_9\}]$ (**11**). The displacement ellipsoids are drawn at the 30% probability level; methyl carbons and hydrogen atoms of the isopropyl groups are omitted for clarity. Selected lengths (Å) and angles (deg): Cd1−O10 = 2.306(10), Cd1−N1 = 2.193(11), O1−Cd1 = 2.313(8), O2−Cd1 = 2.310(8), O3−Cd1 = 2.378(6), O4−Cd1 = 2.407(7), Zr−O = 1.911(8)−2.272(6); O4−Cd1−O10 = 163.8(3), O4−Cd1−N1 = 106.2(4), N1−C1−O10 = 173.7(15), N1−Cd1−O10 = 89.9(5), O4−Cd1−O2 = 70.8(3), O4−Cd1−O1 = 71.4(3), Zr1−O3−Cd1 = 91.0(2), Zr2−O3−Cd2 = 91.1(2).

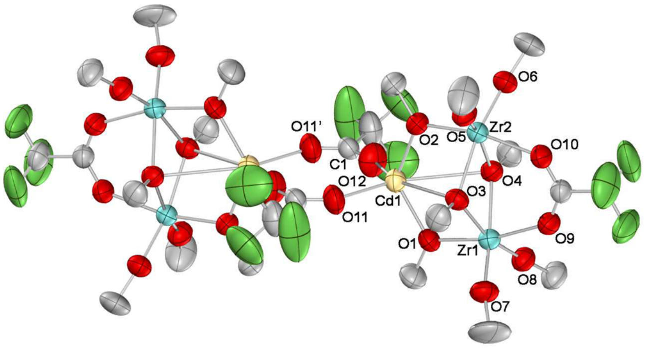


Figure 9. Molecular structure of $[(\mu\text{-}O_2CCF_3)Cd\{Zr_2(OPr^i)_8(O_2CCF_3)\}]_2$ (**9**) (293 K). The displacement ellipsoids are drawn at the 30% probability level; methyl carbons and hydrogen atoms of the isopropyl groups are omitted for clarity. Selected lengths (Å) and angles (deg): Cd1−O12 = 2.197(6), Cd1−O11 = 2.192(5), Cd1−O1 = 2.151(5), Cd1−O2 = 2.147(4), Zr1−O9 = 2.230(5), Zr2−O10 = 2.224(5), $Zr-O_{alkoxide}$ = 1.902(5)−2.209(4); O2−Cd1−O11 = 108.4(2), O2−Cd1−O12 = 105.9(2), O11−C1−O12 = 130.3(8), O3−Zr1−O9 = 84.53(17).

Substitution of metal alkoxides is usually performed by reaction with protic compounds (HY) in which the proton of HY is transferred to an OR group with subsequent elimination of ROH. In a similar manner, an alkoxo group could be transferred to the R′C(O) moiety of the anhydride accompanied by the formation of an ester. However, in these cases neither a protic compound nor an anhydride was involved in the reaction; accidental exposure to moisture cannot be totally excluded. Neither water nor ester could be detected in the reaction mixture. Solution NMR spectroscopic data are not in line with the solid-state structure, but the proposed behavior in solution (Figure 3) could explain the preferred formation of these species in the solid state.

■ CONCLUSION

In the present study the syntheses of new Cd−Zr bimetallic alkoxides based on mixed-ligand systems are reported. In view of the volatility of these compounds, they are potential precursors for deposition of bimetallic oxides by means of chemical vapor deposition. In addition, they are interesting starting materials for the construction of heterotrimetallic alkoxides. We have demonstrated new synthetic approaches for combining M−O−C and M−C derivatives and the introduction of fluorinated ligands. The present investigations represent the beginning of an elusive class of mixed-ligand heterometallic systems. Further studies to establish the generality of the results are currently underway.

The reactions of silver fluoride and trimethyl(perfluoroorgano)silanes offer a convenient and general approach to the synthesis of perfluoroorganosilver(I) compounds. The low toxicity of silver and the ease of recycling make silver compounds attractive for further studies in the field of organic and element-organic synthesis. Finally, it is conceivable that the successful use of argentates to synthesis such heteroleptic heterometallic isopropoxides is an interesting example of incorporating fluorine in a molecular alkoxide assembly, and the extension of this strategy to other metal combinations may provide access to the designing of "single-source" precursors.

■ EXPERIMENTAL SECTION

Chemicals and Methods. All reactions were performed under a nitrogen atmosphere using a modified Stock vacuum line, taking the utmost precautions to prevent adventitious hydrolysis. All reaction vessels were stored in a drying oven at 140 °C before use. Solvents were purified by reported methods.[19] Ammonia was dried by condensation over sodium at −70 °C.

$ZrCl_4$ was purchased from Merck and dried under vacuum prior to use. $[Zr(OPr^i)_4(HOPr^i)]_2$ was prepared by following the ammonia method, as described in the literature.[10] Also, the educts $Cd(C_6F_5)_2{\cdot}2EtCN$[7c] and $Ag(C_6F_5){\cdot}EtCN$[7c] (when not prepared in situ), $Me_3SiC_6F_5$,[20] $Me_3SiC_2F_5$,[20] and $Me_3SiC_6F_4$-4-H[21] were synthesized according to published procedures. Me_3SiCF_3, silver pentafluoropropionate ($AgO_2CC_2F_5$), silver cyanide (AgCN) and silver acetate ($AgCO_2CH_3$) were purchased from ABCR. Silver(I) fluoride (AgF) was purchased from Apollo Scientific Ltd., silver triflate ($AgSO_3CF_3$) and pyridine were obtained from Acros, and CdI_2, Cd powder, silver sulfate (Ag_2SO_4), and benzene were purchased from Merck. Silver(I) acetate ($AgOCOCF_3$) was received from Solvay Fluor and Derivate. Silver perchlorate ($AgClO_4$) and silver cyanate (AgOCN) were purchased from Alfa Aesar; silver nitrate ($AgNO_3$) was obtained from AppliChem. All chemicals were used as received.

NMR spectra were recorded with a Bruker AVANCE II 300 spectrometer at 298 K with NMR spectroscopic frequencies (external standards) as follows: ^{13}C, 75.5 MHz (TMS); ^{19}F, 282.4 MHz (CCl_3F); ^{1}H, 300.1 MHz (TMS); ^{113}Cd, 66 MHz ($Cd(CH_3)_2$, 50% v/v $CDCl_3$). On a Bruker Avance 400 spectrometer at 298 K, NMR spectroscopic frequencies (external standards) were as follows: ^{13}C, 100.61 MHz (TMS); ^{19}F, 376.50 MHz (CCl_3F); ^{1}H, 400.13 MHz (TMS); ^{113}Cd, 88.73 MHz ($Cd(CH_3)_2$). Positive shifts denote downfield resonances. ^{13}C NMR chemical shifts are taken from 1D-^{13}C-APT NMR spectra.

Microanalysis for C, H, N, and S was carried out using a Hekatech CHNS EuroEA 3000 analyzer with helium as carrier gas. The discrepancy between calculated and measured values can be attributed to the high moisture sensitivity of the derivatives. The results for compound **7**, **8**, **11**, **13**, and **14** deviate from the expected analytical purity, and the results provided here refer to the best values obtained after several repetitions. Mass spectra were run on a Thermo Quest Finnigan MAT 95 using electron impact ionization with 20 eV. The isotope patterns for comparison were calculated with the program Isopro,[22] whereby the most intensive peak of the isotope pattern is listed. Melting and decomposition points were determined with a HWS Mainz Laboratoriumstechnik SG 2000 apparatus in sealed 4 mm tubes under an atmosphere of nitrogen and are uncorrected.

TG/DTAs were recorded on a TGA/DSC 1 STAR^e system by Mettler with a GC 100 gas controller. Samples were placed in an aluminum cartridge (HEKAtech GmbH, 5 × 12 mm) and sealed. The measurements were performed under a 25 mL N_2 flow between 40 and 630 °C with a heating rate of 5 °C/min.

Data collections for X-ray crystal structure determination for compounds **3**−**12** were performed on a STOE IPDS I/II diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data were corrected for Lorentz and polarization effects. A numerical absorption correction based on crystal-shape optimization was applied for all data.[23a] The programs used in this work are Stoe's X-Area,[23b] including X-RED and X-Shape for data reduction and absorption correction,[23c] and the WinGX suite of programs,[23d] including SIR-92[23e] and SHELXL-97[23f] for structure solution and refinement. The hydrogen atoms were placed in idealized positions and constrained to ride on their parent atom. The last cycles of refinement included atomic positions for all atoms, anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms. Graphics for publication were prepared using DIAMOND.[23g]

X-ray diffractograms of compound **2** were measured on a Nonius Kappa-CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å), and DENZO was used for data reduction. The structure was solved by direct methods (SHELXS-97[23h]). SHELXL-97[23f] was used for full-matrix least-squares refinement on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in geometrically idealized positions and refined using the riding model.

Selected crystallographic data for compounds **2**−**12** are given in Tables 1−3 in the Supporting Information. CCDC 922612−922622 contain 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.

Synthesis of Precursors. *$[Zr(OPr^i)_4(HOPr^i)]_2$.* This compound was prepared according to the literature procedure.[10] Anal. Found (calcd) for $C_{30}H_{72}O_{10}Zr_2$ (775.34): C, 46.93 (46.47); H, 9.43 (9.36). ^{1}H NMR (400.13 MHz, toluene-d_8, 228 K; δ/ppm): 6.45 (m_{br}, $\Delta_{1/2}$ = 175 Hz, 2H, OH), 5.20 (m, 2H, μ_2 $OC\mathit{H}(CH_3)_2$), 4.48 (m, 4H, axial $OC\mathit{H}(CH_3)_2$), 4.57 (m, 4H, terminal $OC\mathit{H}(CH_3)_2$), 1.70 (d, 12H, μ_2 $OCH(C\mathit{H}_3)_2$), 2.40 (d, 24H, axial $OCH(C\mathit{H}_3)_2$), 1.48 (d, 24H, terminal $OCH(C\mathit{H}_3)_2$). $^{13}C\{^1H\}$ NMR (100.61 MHz, toluene-d_8, 228K; δ/ppm): 71.3 (μ_2 $OCH(CH_3)_2$), 68.3 (axial $OCH(CH_3)_2$), 70.2 (terminal $OCH(CH_3)_2$), 24.9 (μ_2 $OCH(CH_3)_2$), 26.0 (axial $OCH(CH_3)_2$), 27.6 (terminal $OCH(CH_3)_2$). ^{1}H NMR (300.1 MHz, benzene-d_6, 298 K; δ/ppm): 1.50 (d, 60H, $OCH(C\mathit{H}_3)_2$), 4.68 (m, 12H, $OC\mathit{H}(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6, 298 K; δ/ppm): 69.0 ($OCH(CH_3)_2$), 26.2 ($OCH(CH_3)_2$). EI-MS (20 eV; m/z (%)): 821 (47, $[Zr_3(OC_3H_7)_9]^+$), 719 (6, $[Zr_3O_2(OC_3H_7)_7]^+$), 593 (5, $[Zr_3O_3(OC_3H_7)_4(OC_2H_4)_3]^+$), 325 (5, $[Zr(OC_3H_7)_3(OC_3H_6)]^+$), 311 (100, $[Zr(OC_3H_7)_3(OC_2H_4)]^+$), 267 (12, $[Zr(OC_3H_7)_3]^+$), 253 (7, $[Zr(OC_3H_7)_2(OC_2H_4)]^+$), 45 (11, $[OC_2H_5]^+$). Mp: 120−123 °C (glass capillary).

*Iodocadmium Nonaisopropoxydizirconium $[ICd\{Zr_2(OPr^i)_9\}]$ (**1**).* This compound was prepared by the reported method.[3] ^{1}H NMR (300.1 MHz, benzene-d_6, 298 K; δ/ppm): 4.86 (m, 2H, μ_3 $OC\mathit{H}(CH_3)_2$), 4.68 (m, 2H, μ_2 $OC\mathit{H}(CH_3)_2$ (CdZr)), 4.55 (m, 1H, μ_2 $OC\mathit{H}(CH_3)_2$ (ZrZr)), 4.46 (m, 4H, terminal $OC\mathit{H}(CH_3)_2$), 1.66 (d, 12H, μ_3 $OCH(C\mathit{H}_3)_2$), 1.59 (d, 12H, μ_2 $OCH(C\mathit{H}_3)_2$ (CdZr)), 1.45 (d, 6H, μ_2 $OCH(C\mathit{H}_3)_2$ (ZrZr)), 1.37 (d, 24H, terminal $OCH(C\mathit{H}_3)_2$). $^{13}C\{^1H\}$-NMR (75.5 MHz, benzene-d_6, 298 K; δ/ppm): 70.2 (μ_3 $OCH(CH_3)_2$), 70.3 (μ_2 $OCH(CH_3)_2$ (CdZr)), 70.7 (μ_2 $OCH(CH_3)_2$ (ZrZr)), 71.9 (terminal $OCH(CH_3)_2$), 27.2 (μ_3 $OCH(CH_3)_2$ and μ_2 $OCH(CH_3)_2$ (CdZr)), 26.5 (μ_2 $OCH(CH_3)_2$ (ZrZr)), 26.9 (terminal $OCH(CH_3)_2$). ^{113}Cd NMR (66 MHz, benzene-d_6, 298 K; δ/ppm): −593. Mp: 223 °C dec (glass capillary). Anal. Found (calcd) for $C_{27}H_{63}CdIO_9Zr_2$ (953.53): C, 34.35 (34.01); H, 6.89 (6.66). EI-MS (20 eV; m/z (%)): 893 (100, $[ICdZr_2(OC_3H_7)_8]^+$), 767 (8, $[CdZr_2(OC_3H_7)_8]^+$), 653 (8, $[Zr_2(OC_3H_7)_8]^+$), 593 (48, $[Zr_3O_3(OC_3H_7)_4(OC_2H_4)_3]^+$), 566 (50, $[Zr_3O_3(OC_3H_7)_2(OC_2H_4)_3]^+$), 441 (6, $[Zr_3O_5(OC_2H_4)_2]^+$), 368 (8, $[CdI_2]^+$), 325 (9, $[Zr(OPr^i)_3(OC_3H_6)]^+$), 311 (80, [Zr-

$(OC_3H_7)_3(OC_2H_4)]^+$), 267 (13, $[Zr(OC_3H_7)_3]^+$), 253 (10, $[Zr(OC_3H_7)_2(OC_2H_4)]^+$), 45 (32, $[OC_2H_5]^+$). Sublimation temperature: 150 °C/10^{-3} mbar.

General Procedure for the Synthesis of $Ag(C_2F_5)\cdot NC_5H_5$, $Ag(C_6F_4\text{-}4\text{-}H)\cdot NC_5H_5$, and $Ag(C_6F_5)\cdot NC_5H_5$. These compounds were prepared according to the literature procedure for $Ag(C_6F_5)$.[7]

A 0.2 g portion (1.59 mmol) of AgF was suspended in 8 mL of well-dried pyridine at room temperature and the mixture stirred for approximately 15 min. A 2.5 mmol amount (1.5-fold excess) of Me_3SiR_f was added in one portion. Immediately a slightly exothermal reaction started, during which a spotty silver mirror was formed. Stirring was continued overnight. The completeness of the reaction was monitored by ^{19}F NMR spectroscopy, exhibiting the signals of AgR_f in addition to Me_3SiF and low-intensity signals of Me_3SiR_f and R_fH. After decanting, all volatile components were distilled off in vacuo (10^{-3} mbar) at ambient temperature, giving $AgR_f\cdot NC_5H_6$ as a pale gray crystalline material in nearly quantitative (96%) yield.

$AgC_6F_5\cdot NC_5H_5$. ^{19}F NMR (282.4 MHz, acetonitrile-d_3, 298 K; δ/ppm): −105.8 (m, 2 F, F-2,6), −158.4 (t, 1 F, F-4), −163.1 (m, 2 F, F-3,5).

$AgC_2F_5\cdot NC_5H_5$. ^{19}F NMR (282.4 MHz, benzene-d_6, 298 K; δ/ppm): −81.6 (s_{br}, 3 F, CF_2CF_3), −108.2 (s_{br}, 2 F, CF_2CF_3).

$AgC_6F_4\text{-}4\text{-}H\cdot NC_5H_5$. ^{19}F NMR (282.4 MHz, dichloromethane-d_2, 298 K; δ/ppm): −109.8 (m, 2 F, F-2,6), −140.7 (t, 1 F, F-3,5).

General Procedure for the Synthesis of $[(F_5C_6)Cd\{Zr_2(OPr^i)_9\}]$ (2), $[(4\text{-}H\text{-}F_4C_6)Cd\{Zr_2(OPr^i)_9\}]$ (3), and $[(F_5C_2)Cd\{Zr_2(OPr^i)_9\}]$ (4). A solution of 1.5 mmol of AgR_f in pyridine was prepared in situ from Me_3SiR_f and 0.2 g (1.5 mmol) of AgF. After short vacuum evaporation to remove the formed Me_3SiF, a toluene (10 mL) solution of 1.51 g (1.5 mmol) of $[ICd\{Zr_2(OPr^i)_9\}]$ (**1**)[3] was added. Immediately a yellow solid precipitated. After the mixture was stirred overnight and the overlaying supernatant solution was decanted from the precipitated AgI, all volatile components were distilled off under vacuum (1 × 10^{-3} mbar) at room temperature to yield the corresponding derivatives as off-white to pale yellow solids. For all compounds, purity was checked by CHN analysis and mass and ^{19}F, ^{1}H, and ^{13}C NMR spectra.

*Pentafluorophenylcadmium Nonaisopropoxydizirconium, $[(F_5C_6)Cd\{Zr_2(OPr^i)_9\}]$ (**2**).* Yield: 1.46 g (1.47 mmol, 97.5%) crude product (yellowish solid). ^{1}H NMR (300.1 MHz, toluene-d_8, 298 K; δ/ppm): 4.59 (m, 2H, μ_3 OC*H*$(CH_3)_2$ (CdZr)), 4.52 (m, 1H, μ_2 OC*H*$(CH_3)_2$ (ZrZr)), 4.41 (overlapping m, 6H, μ_2 OC*H*$(CH_3)_2$ (CdZr) and terminal OC*H*$(CH_3)_2$), 1.66 (d, 12H, μ_3 OCH$(CH_3)_2$), 1.42 (d, 6H, μ_2 OCH$(CH_3)_2$ (ZrZr)), 1.31 (d, 24H, terminal OCH$(CH_3)_2$), 1.21 (m, 12H, μ_2 OCH$(CH_3)_2$ (CdZr)). ^{13}C{^{1}H} NMR (75.5 MHz, toluene-d_8, 298 K; δ/ppm): 147.8 (C-2,6), 136.9 (C-3,5), 140.3 (C-1), 120.0 (C-4), 70.3 (μ_3 OCH$(CH_3)_2$), 69.6 (μ_2 OCH$(CH_3)_2$ (CdZr)), 70.1 (μ_2 OCH$(CH_3)_2$ (ZrZr)), 71.8 (terminal OCH$(CH_3)_2$), 27.1 (μ_3 OCH$(CH_3)_2$), 27.1 (μ_2 OCH$(CH_3)_2$ (CdZr)), 26.2 (μ_2 OCH$(CH_3)_2$ (ZrZr)), 26.7 (terminal OCH$(CH_3)_2$). ^{19}F NMR (282.4 MHz, toluene-d_8, 298 K; δ/ppm): −110.0 (m, 2F, F-3,5), −154.5 (m, 1F, F-4), −159.7 (m, 2F, F-2,6). ^{19}F NMR spectra in all solvents exhibit the characteristic splitting of a pentafluorophenyl group (AA′MM′X spin system). ^{113}Cd NMR (66 MHz, toluene-d_8, 298 K; δ/ppm): −465. Mp: 158 °C (glass capillary). Anal. Found (calcd) for $C_{33}H_{63}CdF_5O_9Zr_2$ (993.69): C, 40.03 (39.89); H, 6.40 (6.39). EI-MS (20 eV; *m/z* (%)): 932 (100, $[C_6F_6CdZr_2(OC_3H_7)_7]^+$), 919 (8, $[C_6F_5CdZr_2(OC_3H_7)_8]^+$), 820 (6, $[Zr_3(OC_3H_7)_9]^+$), 765 (9, $[CdZr_2(OC_3H_7)_8]^+$), 650 (7, $[Zr_2(OC_3H_7)_8]^+$), 606 (55, $[C_6F_5CdZr(OC_3H_7)_4]^+$), 593 (50, $[Zr_3O_3(OC_3H_7)_4(OC_2H_4)_3]^+$), 566 (4, $[Zr_3O_3(OC_3H_7)_2(OC_2H_4)_3]^+$), 311 (43, $[Zr(OC_3H_7)_3(OC_2H_4)]^+$), 168 (10, $[C_6F_5H]^+$), 45 (10, $[OC_2H_5]^+$). Sublimation temperature: 140 °C/10^{-3} mbar.

*Alternative Synthesis of $[(F_5C_6)Cd\{Zr_2(OPr^i)_9\}]$ (**2**) through an Acid–Base Reaction.* A toluene (30 mL) solution of $[Zr(OPr^i)_4(HOPr^i)]_2$ (1.0 g, 1.29 mmol) was added to a well-stirred suspension of $Cd(C_6F_5)_2\cdot 2EtCN$ (0.72 g, 1.29 mmol) in toluene. Stirring was continued overnight at room temperature. The clear solution obtained was evaporated to dryness in vacuo (1 × 10^{-3} mbar), giving a pale yellow solid in nearly quantitative yield (96%).

*4-H-tetrafluorophenylcadmium Nonaisopropoxydizirconium, $[(4\text{-}H\text{-}F_4C_6)Cd\{Zr_2(OPr^i)_9\}]$ (**3**).* Yield: 1.43 g (1.47 mmol, 92.5%) crude product (yellowish solid). ^{1}H NMR (300.1 MHz, toluene-d_8, 298 K; δ/ppm): 6.6 (m, 1H, 4-*H*-C_6F_4), 4.77 and 4.69 (overlapping m, total integral of 4H, μ_3 OC*H*$(CH_3)_2$ and μ_2 OC*H*$(CH_3)_2$ (CdZr)), 4.52 (overlapping m_{br}, total integral of 5H, μ_2 OC*H*$(CH_3)_2$ (ZrZr) and terminal OC*H*$(CH_3)_2$), 1.77 and 1.61 (overlapping d, total integral of 4H, μ_3 OCH$(CH_3)_2$ and μ_2 OCH$(CH_3)_2$ (CdZr)), 1.40 (overlapping d, total integral of 5H, μ_2 OCH$(CH_3)_2$ (ZrZr) and terminal OCH$(CH_3)_2$). ^{13}C{^{1}H NMR (75.5 MHz, toluene-d_8, 298 K; δ/ppm): 148.8 (C-2,6), 146.0 (C-3,5), 129.1 (C-1), 106.4 (C-4), 70.7 and 70.0 (μ_3 OCH$(CH_3)_2$ and μ_2 OCH$(CH_3)_2$ (CdZr)), 71.3 (μ_2 OCH$(CH_3)_2$ (ZrZr) and terminal OCH$(CH_3)_2$), 26.5 and 26.3 (μ_3 OCH$(CH_3)_2$ and μ_2 OCH$(CH_3)_2$ (CdZr)), 26.1 (μ_2 OCH$(CH_3)_2$ (ZrZr) and terminal OCH$(CH_3)_2$). ^{19}F NMR (282.4 MHz, toluene-d_8, 298 K; δ/ppm): −110.9 (m, 2 F, F-2,6), −138.1 (m, 2 F, F-3,5). ^{113}Cd NMR (66.0 MHz, toluene-d_8, 298 K; δ/ppm): −468. Anal. Found (calcd) for $C_{33}H_{64}CdF_4O_9Zr_2$ (975.7): C, 40.23 (40.62); H, 6.89 (6.61). EI-MS (20 eV; *m/z* (%)): 915 (70, $[C_6F_5HCdZr_2(OC_3H_7)_8]^+$), 766 (10, $[C_6F_5CdZr_2(OC_3H_7)_7O]^+$), 651 (5, $[Zr_2(OC_3H_7)_8]^+$), 593 (68, $[Zr_3O_3(OC_3H_7)_4(OC_2H_4)_3]^+$), 587 (66, $[C_6F_4HCdZr(OC_3H_7)_4]^+$), 325 (8, $[Zr(OC_3H_7)_3(OC_3H_6)]^+$), 311 (21, $[Zr(OC_3H_7)_3(OC_2H_4)]^+$), 150 (23, $[C_6F_4H]^+$), 45 (100, $[OC_2H_5]^+$). Sublimation temperature: 155 °C/10^{-3} mbar.

*Pentafluoroethylcadmium Nonaisopropoxydizirconium, $[(F_5C_2)Cd\{Zr_2(OPr^i)_9\}]$ (**4**).* Yield: 1.48 g (1.57 mmol, 98.1%) crude product (white solid). ^{1}H NMR (400.13 MHz, benzene-d_6, 298 K; δ/ppm): 4.69 (m, 2H, μ_3 OC*H*$(CH_3)_2$), 4.56 (overlapping m, total integral of 7H, μ_2 OC*H*$(CH_3)_2$ (CdZr) and μ_2 OC*H*$(CH_3)_2$ (ZrZr) and terminal OC*H*$(CH_3)_2$), 1.46 (overlapping d, total integral of 5H, μ_3 OCH$(CH_3)_2$) and μ_2 OCH$(CH_3)_2$ (CdZr) and μ_2 OCH$(CH_3)_2$ (ZrZr)), 1.45 (d, 4H, terminal OCH$(CH_3)_2$). ^{13}C{^{1}H} NMR (100.61 MHz, benzene-d_6, 298 K; δ/ppm): 135.3 ($CdCF_2CF_3$), 122.8 ($CdCF_2CF_3$), 71.9 (μ_3 OCH$(CH_3)_2$ and μ_2 OCH$(CH_3)_2$ (CdZr) and μ_2 OCH$(CH_3)_2$ (ZrZr)), 69.9 (terminal OCH$(CH_3)_2$), 26.7 (μ_3 OCH$(CH_3)_2$ and μ_2 OCH$(CH_3)_2$ (CdZr) and μ_2 OCH$(CH_3)_2$ (ZrZr) and terminal OCH$(CH_3)_2$). ^{19}F NMR (376.5 MHz, benzene-d_6, 298 K): δ = −118.9 (t, 2 F, CF_2CF_3), −85.4 (m, 3 F, CF_2CF_3). ^{113}Cd NMR (88.73 MHz, benzene-d_6, 298 K; δ/ppm): −532. Mp: 168 °C (glass capillary) (onset of decomposition at 142 °C). Anal. Found (calcd) for $C_{29}H_{63}CdF_5O_9Zr_2$ (945.65): C, 37.18 (36.83); H, 6.63 (6.72). EI-MS (20 eV; *m/z* (%)): 885 (100, $[C_2F_5CdZr_2(OC_3H_7)_8]^+$), 821 (8, $[Zr_3(OC_3H_7)_9]^+$), 767 (20, $[CdZr_2(OC_3H_7)_8]^+$), 651 (7, $[Zr_2(OC_3H_7)_8]^+$), 593 (52, $[Zr_3O_3(OC_3H_7)4(OC_2H_4)_3]^+$), 559 (68, $[CdZrC_2F_5(OC_3H_7)_4]^+$), 441 (12, $[Zr_3O_5(OC_2H_4)_2]^+$), 325 (9, $[Zr(OC_3H_7)_3(OC_3H_6)]^+$), 311 (38, $[Zr(OC_3H_7)_3(OC_2H_4)]^+$). Sublimation temperature: 145 °C/10^{-3} mbar.

General Procedure for the Synthesis of $[(ONO_2)Cd\{Zr_2(OPr^i)_9\}]_2$ (5), $[(CH_3CO_2)Cd\{Zr_2(OPr^i)_9\}]$ (6), $[(O_2ClO_2)(H_5C_3N)Cd\{Zr_2(OPr^i)_9\}]$ (7), $[(\mu\text{-}O_2ClO_2)Cd\{Zr_2(OPr^i)_9\}]_2$ (8), $[(\mu\text{-}O_2CCF_3)Cd\{Zr_2(OPr^i)_8(O_2CCF_3)\}]_2$ (9), $[(\mu\text{-}O_2CC_2F_5)Cd\{Zr_2(OPr^i)_8(O_2CC_2F_5)\}]_2$ (10), $[(\mu(O,N)\text{-}OCN)Cd\{Zr_2(OPr^i)_9\}]_2$ (11), $[(\mu\text{-}O_2SOCF_3)Cd\{Zr_2(OPr^i)_9\}]_2$ (12), $[(NC)Cd\{Zr_2(OPr^i)_9\}]$ (13), and $[(SO_4)\{Cd\{Zr_2(OPr^i)_9\}\}_2]$ (14). One equivalent of $[ICd\{Zr_2(OPr^i)_9\}]$ (**1**)[3] in a heptane/toluene mixture was added to a well-stirred suspension of AgR in propionitrile/toluene. Directly after combination, a yellow precipitate was formed. The mixture was stirred for 12 h and decanted, and the volume of the solution was reduced by slow evaporation of all volatiles. In the synthesis of **8** and **14** no propionitrile was involved and the reaction time was prolonged to 3 days.

*(Nitrato)cadmium Nonaisopropoxydizirconium, $[(ONO_2)Cd\{Zr_2(OPr^i)_9\}]$ (**5**).* Educts: $[ICd\{Zr_2(OPr^i)_9\}]$ (0.34 g, 0.35 mmol), $Ag(NO_3)$ (0.06 g, 0.35 mmol). Yield: 0.29 g (0.33 mmol, 92.6%) crude product (white solid). ^{1}H NMR (300.1 MHz, benzene-d_6, 298 K; δ/ppm): 4.63 and 4.59 (overlapping m, 4H, μ_3 OC*H*$(CH_3)_2$ and μ_2 OC*H*$(CH_3)_2$ (CdZr)), 4.47 (m, 1H, μ_2 OC*H*$(CH_3)_2$ (ZrZr)), 4.43 (m, 4H, terminal OC*H*$(CH_3)_2$), 1.59 and 1.41 (overlapping d, 24H, μ_3 OCH$(CH_3)_2$ and μ_2 OCH$(CH_3)_2$ (CdZr)), 1.40 (overlapping d, 18H,

μ_2 $\mathrm{OCH(C}H_3)_2$ (ZrZr) and terminal $\mathrm{OCH(C}H_3)_2$), 1.34 (d, 12H, terminal $\mathrm{OCH(C}H_3)_2$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (75.5 MHz, benzene-d_6, 298 K; δ/ppm): 70.6 (μ_3 $\mathrm{OCH(CH_3)_2}$), 69.8 (μ_2 $\mathrm{OCH(CH_3)_2}$ (CdZr)), 70.5 (μ_2 $\mathrm{OCH(CH_3)_2}$ (ZrZr)), 72.0 (terminal $\mathrm{OCH(CH_3)_2}$), 27.0 (μ_3 $\mathrm{OCH(CH_3)_2}$) 26.4 (μ_2 $\mathrm{OCH(CH_3)_2}$ (CdZr)), 26.5 (μ_2 $\mathrm{OCH(CH_3)_2}$ (ZrZr)), 26.7 (terminal $\mathrm{OCH(CH_3)_2}$). ^{113}Cd NMR (66 MHz, benzene-d_6, 298 K; δ/ppm): −658. Anal. Found (calcd) for $\mathrm{C_{27}H_{63}CdNO_{12}Zr_2}$ (888.64): C, 36.79 (36.49); H, 7.70 (7.15); N, 1.47 (1.58). EI-MS (20 eV; m/z (%)): 828 (35, $[\mathrm{CdZr_2(NO_3)(OC_3H_7)_8}]^+$), 821 (18, $[\mathrm{Zr_3(OC_3H_7)_9O}]^+$), 770 (44, $[\mathrm{CdZr_2(NO_3)(OC_3H_7)_7}]^+$), 665 (27, $[\mathrm{CdZr_2O_2(OC_3H_7)_5(NO_2)}]^+$), 593 (40, $[\mathrm{Zr_3O_3(OC_3H_7)_4(OC_2H_4)_3}]^+$), 441 (32, $[\mathrm{Zr_3O_5(OC_2H_4)_2}]^+$), 325 (10, $[\mathrm{Zr(OC_3H_7)_3(OC_3H_6)}]^+$), 311 (100, $[\mathrm{Zr(OC_3H_7)_3(OC_2H_4)}]^+$), 267 (13, $[\mathrm{Zr(OC_3H_7)_3}]^+$), 253 (8, $[\mathrm{Zr(OC_3H_7)_2(OC_2H_4)}]^+$), 58 (8, $[\mathrm{C_2H_4N}]^+$), 45 (80, $[\mathrm{OC_2H_5}]^+$). Sublimation temperature: 150 °C/10^{-3} mbar.

*(Acetato)cadmium Nonaisopropoxydizirconium, $[(\mathrm{CH_3CO_2})\mathrm{Cd}\{\mathrm{Zr_2(OPr}^i)_9\}]$ (**6**).* Educts: $[\mathrm{ICd}\{\mathrm{Zr_2(OPr}^i)_9\}]$ (1.14 g, 1.2 mmol), $\mathrm{AgOCOCH_3}$ (0.2 g, 1.2 mmol). Yield: 1.02 g (1.15 mmol, 97.9%) crude product (white solid). ^{1}H NMR (300.1 MHz, benzene-d_6, 298 K; δ/ppm): 4.72 and 4.70 (overlapping m, 4H, μ_3 $\mathrm{OC}H\mathrm{(CH_3)_2}$ and μ_2 $\mathrm{OC}H\mathrm{(CH_3)_2}$ (CdZr)), 4.55 (m, 1H, μ_2 $\mathrm{OC}H\mathrm{(CH_3)_2}$ (ZrZr)), 4.51 (m, 4H, terminal $\mathrm{OC}H\mathrm{(CH_3)_2}$), 2.25 (s, 3H, $\mathrm{O_2CC}H_3$), 1.75 and 1.53 (d, 12H, μ_3 $\mathrm{OCH(C}H_3)_2$ and μ_2 $\mathrm{OCH(C}H_3)_2$ (CdZr)), 1.48 (d (overlapping with resonance at 1.53), 6H, μ_2 $\mathrm{OCH(C}H_3)_2$ (ZrZr)), 1.38 (dd, 24H, terminal $\mathrm{OCH(C}H_3)_2$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$-NMR (75.5 MHz, benzene-$d_6$, 298 K; δ/ppm): 181.2 ($\mathrm{O_2CCH_3}$), 70.6 (μ_3 $\mathrm{OCH(CH_3)_2}$), 70.2 (μ_2 $\mathrm{OCH(CH_3)_2}$ (CdZr)), 71.4 (μ_2 $\mathrm{OCH(CH_3)_2}$ (ZrZr)), 71.7 (terminal $\mathrm{OCH(CH_3)_2}$), 26.4 (μ_3 $\mathrm{OCH(CH_3)_2}$), 27.1 (μ_2 $\mathrm{OCH(CH_3)_2}$ (CdZr)), 26.6 (μ_2 $\mathrm{OCH(CH_3)_2}$ (ZrZr)), 26.9 (terminal $\mathrm{OCH(CH_3)_2}$), 20.6 ($\mathrm{O_2CCH_3}$). ^{113}Cd NMR (66 MHz, benzene-d_6, 298 K; δ/ppm): −643. Anal. Found (calcd) for $\mathrm{C_{28}H_{66}CdO_{11}Zr_2}$ (885.68): C, 39.54 (39.33); H, 7.50 (7.51). EI-MS (20 eV; m/z (%)): 825 and 821 (39, $[(\mathrm{O_2CCH_3})\mathrm{CdZr_2(OC_3H_7)_8}]^+$ and $[\mathrm{Zr_3(OC_3H_7)_9O}]^+$), 768 and 767 (58, $[(\mathrm{O_2CCH_3})\mathrm{CdZr_2(OC_3H_7)_7}]^+$ and $[\mathrm{CdZr_2(OC_3H_7)_8}]^+$), 593 (12, $[\mathrm{Zr_3O_3(OC_3H_7)_4(OC_2H_4)_3}]^+$), 499 (11, $[(\mathrm{O_2CCH_3})\mathrm{CdZr(OC_3H_7)_4}]^+$), 440 (38, $[\mathrm{Zr_3O_5(OC_2H_4)_2}]^+$), 311 (41, $[\mathrm{Zr(OC_3H_7)_3(OC_2H_4)}]^+$), 267 (8, $[\mathrm{Zr(OC_3H_7)_3}]^+$), 45 (100, $[\mathrm{OC_2H_5}]^+$). Sublimation temperature: 155 °C/10^{-3} mbar.

*Propionitrilo(perchlorato)cadmium Nonaisopropoxydizirconium, $[(\mathrm{O_2ClO_2})(\mathrm{H_5C_3N})\mathrm{Cd}\{\mathrm{Zr_2(OPr}^i)_9\}]$ (**7**).* Educts: $[\mathrm{ICd}\{\mathrm{Zr_2(OPr}^i)_9\}]$ (1.53 g, 1.6 mmol), $\mathrm{Ag(ClO_4)}$ (0.33 g, 1.6 mmol). Yield: 1.38 g (1.41 mmol, 88%) crude product (yellowish solid). ^{1}H NMR (300.1 MHz, benzene-d_6, 298 K; δ/ppm): 4.70 (m, 2H, μ_3 $\mathrm{OC}H\mathrm{(CH_3)_2}$), 4.60 (m, 2H, μ_2 $\mathrm{OC}H\mathrm{(CH_3)_2}$ (CdZr)), 4.50 (m, 1H, μ_2 $\mathrm{OC}H\mathrm{(CH_3)_2}$ (ZrZr)), 4.50 (m, 4H, terminal $\mathrm{OC}H\mathrm{(CH_3)_2}$), 1.60 (d, 12H, μ_3 $\mathrm{OCH(C}H_3)_2$), 1.70 (d, 12H, μ_2 $\mathrm{OCH(C}H_3)_2$ (CdZr)), 1.40 (overlapping d, 30H, μ_2 $\mathrm{OCH(C}H_3)_2$ (ZrZr) and terminal $\mathrm{OCH(C}H_3)_2$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (75.5 MHz, benzene-d_6, 298 K; δ/ppm): 70.0 (μ_3 $\mathrm{OCH(CH_3)_2}$), 70.9 (μ_2 $\mathrm{OCH(CH_3)_2}$ (CdZr)), 70.5 (μ_2 $\mathrm{OCH(CH_3)_2}$ (ZrZr)), 72.0 (terminal $\mathrm{OCH(CH_3)_2}$), 27.0 (μ_3 $\mathrm{OCH(CH_3)_2}$), 26.3 (μ_2 $\mathrm{OCH(CH_3)_2}$ (CdZr)), 26.6 (μ_2 $\mathrm{OCH(CH_3)_2}$ (ZrZr)), 26.7 and 26.6 (terminal $\mathrm{OCH(CH_3)_2}$). ^{113}Cd NMR (66 MHz, benzene-d_6, 298 K; δ/ppm): −673. Anal. Found (calcd) for $\mathrm{C_{30}H_{68}CdClNO_{13}Zr_2}$ (981.16): C, 35.73 (36.72), H, 7.63 (6.99); N, 1.02 (1.43). EI-MS (20 eV; m/z (%)): 981 (3, $[\mathrm{CdZr_2(ClO_4)(NC_3H_7)(OC_3H_7)_9}^+]$ +), 951 (7, $[\mathrm{Zr_3(OC_3H_7)_{11}(OCH_2)}]^+$), 901 (23, $[\mathrm{Zr_4O_4(OC_3H_7)_8}]^+$), 861 (6, $[\mathrm{Zr_3O(OC_3H_7)_9(OC_2H_5)}]^+$), 801 (17, $[\mathrm{Zr_3O(OC_3H_7)_8(OC_2H_5)}]^+$), 593 (5, $[\mathrm{Zr_3O_3(OC_3H_7)_4(OC_2H_4)_3}]^+$), 58 (37, $[\mathrm{C_2H_4N}]^+$), 45 (100, $[\mathrm{OC_2H_5}]^+$).

*Bis(perchlorato)cadmium Nonaisopropoxydizirconium, $[(\mu\text{-}\mathrm{O_2ClO_2})\mathrm{Cd}\{\mathrm{Zr_2(OPr}^i)_9\}]_2$ (**8**).* Educts: $[\mathrm{ICdZr_2(OPr}^i)_9]$ (2.00 g, 2.1 mmol), $\mathrm{Ag(ClO_4)}$ (0.43 g, 2.1 mmol). Yield: 1.61 g (1.74 mmol, 83%) crude product (yellowish solid). ^{1}H NMR (300.1 MHz, benzene-d_6, 298 K; δ/ppm): 4.7 (m, 2H, μ_3 $\mathrm{OC}H\mathrm{(CH_3)_2}$), 4.60 (m, 2H, μ_2 $\mathrm{OC}H\mathrm{(CH_3)_2}$ (CdZr)), 4.50 (m, 1H, μ_2 $\mathrm{OC}H\mathrm{(CH_3)_2}$ (ZrZr)), 4.41 (m, 4H, terminal $\mathrm{OC}H\mathrm{(CH_3)_2}$), 1.60 (d, 12H, μ_3 $\mathrm{OCH(C}H_3)_2$), 1.56 (d, 12H, μ_2 $\mathrm{OCH(C}H_3)_2$ (CdZr)), 1.40 (d, 6H, μ_2 $\mathrm{OCH(C}H_3)_2$ (ZrZr)), 1.32 (d, 24H, terminal $\mathrm{OCH(C}H_3)_2$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (75.5 MHz, benzene-d_6, 298 K; δ/ppm): 70.3 (μ_3 $\mathrm{OCH(CH_3)_2}$), 70.7 (μ_2 $\mathrm{OCH(CH_3)_2}$ (CdZr)), 70.6 (μ_2 $\mathrm{OCH(CH_3)_2}$ (ZrZr)), 72.2 (terminal $\mathrm{OCH(CH_3)_2}$), 27.0 (μ_3 $\mathrm{OCH(CH_3)_2}$), 26.4 (μ_2 $\mathrm{OCH(CH_3)_2}$ (CdZr)), 26.5 (μ_2 $\mathrm{OCH(CH_3)_2}$ (ZrZr)), 26.6 (terminal $\mathrm{OCH(CH_3)_2}$). ^{113}Cd NMR (66 MHz, benzene-d_6, 298 K; δ/ppm): −688. Anal. Found (calcd) for $\mathrm{C_{27}H_{63}CdClO_{13}Zr_2}$ (926.08): C, 33.21 (35.02); H, 7.02 (6.86). EI-MS (20 eV; m/z (%)): 867 (78, $[\mathrm{CdZr_2(ClO_4)(OC_3H_7)_8}]^+$), 805 (45, $[\mathrm{Zr_3O(OC_3H_7)_8(OC_2H_5)}]^+$), 767 (8, $[\mathrm{CdZr_2(OC_3H_7)_8}]^+$), 593 (100, $[\mathrm{Zr_3O_3(OC_3H_7)_4(OC_2H_4)_3}]^+$), 567 (8, $[\mathrm{Zr_3O_3(OC_3H_7)_2(OC_2H_4)_3}]^+$), 475 (13, $[(\mathrm{ClO_4})\mathrm{CdZr(OC_3H_7)_4}]^+$), 441 (46, $[\mathrm{Zr_3O_5(OC_2H_4)_2}]^+$), 325 (10, $[\mathrm{Zr(OC_3H_7)_3(OC_3H_6)}]^+$), 311 (100, $[\mathrm{Zr(OC_3H_7)_3(OC_2H_4)}]^+$), 267 (11, $[\mathrm{Zr(OC_3H_7)_3}]^+$), 253 (9, $[\mathrm{Zr(OC_3H_7)_2(OC_2H_4)}]^+$), 58 (10, $[\mathrm{C_2H_4N}]^+$), 45 (44, $[\mathrm{OC_2H_5}]^+$).

*Bis(trifluoroacetato)cadmium Octaisopropoxy(trifluoroacetato)dizirconium, $[(\mu\text{-}\mathrm{O_2CCF_3})\mathrm{Cd}\{\mathrm{Zr_2(OPr}^i)_8(\mathrm{O_2CCF_3})\}]_2$ (**9**).* Educts: $[\mathrm{ICd}\{\mathrm{Zr_2(OPr}^i)_9\}]$ (0.55 g, 0.58 mmol), $\mathrm{Ag(O_2CCF_3)}$ (0.14 g, 0.58 mmol). Yield: 0.32 g (0.34 mmol, 59%) crude product (white solid). ^{1}H NMR (300.1 MHz, benzene-d_6, 298 K; δ/ppm): 4.55 (m, 4H, μ_3 $\mathrm{OC}H\mathrm{(CH_3)_2}$ and μ_2 $\mathrm{OC}H\mathrm{(CH_3)_2}$ (CdZr)), 4.44 and 4.34 (overlapping m, 5H, μ_2 $\mathrm{OC}H\mathrm{(CH_3)_2}$ (ZrZr) and terminal $\mathrm{OC}H\mathrm{(CH_3)_2}$), 1.57 (d, 12H, μ_3 $\mathrm{OCH(C}H_3)_2$), 1.36 (overlapping d, 18H, μ_2 $\mathrm{OCH(C}H_3)_2$ (CdZr) and μ_2 $\mathrm{OCH(C}H_3)_2$ (ZrZr)) 1.28 (dd, 24H, terminal $\mathrm{OCH(C}H_3)_2$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (75.5 MHz, benzene-d_6, 298 K; δ/ppm): 166.1 ($\mathrm{O_2CCF_3}$), 117.4 ($\mathrm{O_2CCF_3}$), 70.3 (μ_3 $\mathrm{OCH(CH_3)_2}$), 70.7 (μ_2 $\mathrm{OCH(CH_3)_2}$ (CdZr)), 70.6 (μ_2 $\mathrm{OCH(CH_3)_2}$ (ZrZr)), 72.2 (terminal $\mathrm{OCH(CH_3)_2}$), 27.0 (μ_3 $\mathrm{OCH(CH_3)_2}$), 26.4 (μ_2 $\mathrm{OCH(CH_3)_2}$ (CdZr)), 26.5 (μ_2 $\mathrm{OCH(CH_3)_2}$ (ZrZr)), 26.6 (terminal $\mathrm{OCH(CH_3)_2}$). ^{113}Cd NMR (66 MHz, benzene-d_6, 298 K; δ/ppm): −650. ^{19}F NMR (282.4 MHz, benzene-d_6, 298 K; δ/ppm): −73.3. Anal. Found (calcd; sublimed product) for $\mathrm{C_{29}H_{63}CdF_3O_{11}Zr_2}$ (939.65): C, 37.15 (37.07); H, 7.49 (6.76). EI-MS (20 eV; m/z (%)): 879 (100, $[(\mathrm{O_2CCF_3})\mathrm{CdZr_2(OC_3H_7)_8}]^+$), 821 (100, $[\mathrm{Zr_3(OC_3H_7)_9O}]^+$), 766 (17, $[\mathrm{CdZr_2(OC_3H_7)_8}]^+$), 593 (37, $[\mathrm{Zr_3O_3(OC_3H_7)_4(OC_2H_4)_3}]^+$), 567 (9, $[\mathrm{Zr_3O_3(OC_3H_7)_2(OC_2H_4)_3}]^+$), 553 (18, $[(\mathrm{O_2CCF_3})\mathrm{CdZr(OC_3H_7)_4}]^+$), 440 (52, $[\mathrm{Zr_3O_5(OC_2H_4)_2}]^+$), 325 (12, $[\mathrm{Zr(OC_3H_7)_3(OC_3H_6)}]^+$), 311 (46, $[\mathrm{Zr(OC_3H_7)_3(OC_2H_4)}]^+$), 45 (93, $[\mathrm{OC_2H_5}]^+$). Anal. Found (calcd; crystallized product) for $\mathrm{C_{28}H_{56}CdF_6O_{12}Zr_2}$ (993.58): C, 33.81 (33.85); H, 6.98 (5.68); N, 1.25 (0). EI-MS (20 eV; m/z (%)): 933 (28, $[(\mathrm{CO_2CF_3})_2\mathrm{CdZr_2(OC_3H_7)_7}]^+$), 879 (100, $[(\mathrm{O_2CCF_3})\mathrm{CdZr_2(OC_3H_7)_8}]^+$), 821 (100, $[\mathrm{Zr_3(OC_3H_7)_9O}]^+$), 766 (17, $[\mathrm{CdZr_2(OC_3H_7)_8}]^+$), 593 (37, $[\mathrm{Zr_3O_3(OC_3H_7)_4(OC_2H_4)_3}]^+$), 553 (18, $[(\mathrm{O_2CCF_3})\mathrm{CdZr(OC_3H_7)_4}]^+$), 440 (52, $[\mathrm{Zr_3O_5(OC_2H_4)_2}]^+$), 311 (46, $[\mathrm{Zr(OC_3H_7)_3(OC_2H_4)}]^+$), 58 (9, $[\mathrm{C_2H_4N}]^+$), 45 (93, $[\mathrm{OC_2H_5}]^+$). Sublimation temperature: 145 °C/10^{-3} mbar.

*Bis(pentafluoropropionato)cadmium Octaisopropoxy(pentafluoropropionato)dizirconium, $[(\mu\text{-}\mathrm{O_2CC_2F_5})\mathrm{Cd}\{\mathrm{Zr_2(OPr}^i)_8(\mathrm{O_2CC_2F_5})\}]_2$ (**10**).* Educts: $[\mathrm{ICd}\{\mathrm{Zr_2(OPr}^i)_9\}]$ (1.781 g, 1.88 mmol), $\mathrm{Ag(O_2CC_2F_5)}$ (0.506 g, 1.88 mmol). Yield: 1.01 g (1.02 mmol, 54%) crude product (yellowish waxy solid). ^{1}H NMR (300.1 MHz, benzene-d_6, 298 K; δ/ppm): 4.66 and 4.59 (overlapping m, 4H, μ_3 $\mathrm{OC}H\mathrm{(CH_3)_2}$ and μ_2 $\mathrm{OC}H\mathrm{(CH_3)_2}$ (CdZr)), 4.49 and 4.45 (overlapping m, 5H, μ_2 $\mathrm{OC}H\mathrm{(CH_3)_2}$ (ZrZr) and terminal $\mathrm{OC}H\mathrm{(CH_3)_2}$), 1.64 (d, 12H, μ_3 $\mathrm{OCH(C}H_3)_2$), 1.39 and 1.41 (overlapping d, 18H, μ_2 $\mathrm{OCH(C}H_3)_2$ (CdZr) and μ_2 $\mathrm{OCH(C}H_3)_2$ (ZrZr)), 1.35 (dd, 24H, terminal $\mathrm{OCH(C}H_3)_2$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (75.5 MHz, benzene-d_6, 298 K; δ/ppm): 181.9 ($\mathrm{O_2CC_2F_5}$), 133.9 ($\mathrm{O_2CCF_2CF_3}$), 123.1 ($\mathrm{O_2CCF_2CF_3}$), 69.8 (μ_3 $\mathrm{OCH(CH_3)_2}$), 70.5 (μ_2 $\mathrm{OCH(CH_3)_2}$ (CdZr)), 70.4 (μ_2 $\mathrm{OCH(CH_3)_2}$ (ZrZr)), 71.8 (terminal $\mathrm{OCH(CH_3)_2}$), 26.8 (μ_3 $\mathrm{OCH(CH_3)_2}$), 26.4 (μ_2 $\mathrm{OCH(CH_3)_2}$ (CdZr)), 26.5 (μ_2 $\mathrm{OCH(CH_3)_2}$ (ZrZr)), 26.6 (terminal $\mathrm{OCH(CH_3)_2}$). ^{19}F NMR (282.4 MHz, benzene-d_6, 298 K; δ/ppm): −118.9 (s$_{\mathrm{br}}$, 2F, $\mathrm{O_2CC}F_2\mathrm{CF_3}$), −82.6 (s$_{\mathrm{br}}$, 3F, $\mathrm{O_2CCF_2C}F_3$). ^{113}Cd NMR (66 MHz, benzene-d_6, 298 K; δ/ppm): −651. Anal. Found (calcd; sublimed product) for $\mathrm{C_{30}H_{63}CdF_5O_{11}Zr_2}$ (989.66): C, 36.36 (36.41); H, 7.49 (6.42). Found (calcd; crystallized product) for $\mathrm{C_{30}H_{56}CdF_{10}O_{12}Zr_2}$ (1093.59): C, 34.29 (32.95); H, 4.16 (5.16). EI-MS (20 eV; m/z (%)):1032 (50, $[\mathrm{CdZr_2(OC_3H_7)_7(C_2F_5CO_2)_2}]^+$), 974 (10, $[\mathrm{CdZr_2(OC_3H_7)_6(OC_2H_4)(C_2F_5CO_2)(C_2F_5)}]^+$), 951 (8,

$[Zr_3(OC_3H_7)_{11}(OCH_2)]^+$), 929 (100, $[CdZr_2(OC_3H_7)_8(C_2F_5CO_2)]^+$), 871 (37, $[CdZr_2(OC_3H_7)_7(C_2F_5CO_2)]^+$ and $[Zr_3O(OC_3H_7)_9(OC_2H_5)]^+$), 847 (74, $[Zr_3O(OC_3H_7)_9(OCH_3)]^+$), 821 (24, $[Zr_3(OC_3H_7)_9O]^+$), 766 (9, $[CdZr_2(OC_3H_7)_8]^+$), 697 (24, $[Zr_2(OC_3H_7)_6(O_2CC_2F_5)]^+$), 593 (69, $[Zr_3O_3(OC_3H_7)_4(OC_2H_4)_3]^+$), 567 (12, $[Zr_3O_3(OC_3H_7)_2(OC_2H_4)_3]^+$), 519 (28, ?), 440 (46, $[Zr_3O_5(OC_2H_4)_2]^+$), 325 (13, $[Zr(OC_3H_7)_3(OC_3H_6)]^+$), 311 (38, $[Zr(OC_3H_7)_3(OC_2H_4)]^+$), 45 (93, $[OC_2H_5]^+$). Sublimation temperature: 145 °C/10^{-3} mbar.

*Bis(cyanato)cadmium Nonaisopropoxydizirconium, $[(\mu(O,N)\text{-}OCN)Cd\{Zr_2(OPr^i)_9\}]_2$ (**11**).* Educts $[ICd\{Zr_2(OPr^i)_9\}]$ (1.00 g, 1.05 mmol), Ag(OCN) (0.16 g, 1.05 mmol). Yield: 0.56 g (0.64 mmol, 61.4%) crude product (yellowish solid). ^1H NMR (300.1 MHz, benzene-d_6, 298 K; δ/ppm): 4.55 (m_{br}, 3H, μ_3 $OC\mathit{H}(CH_3)_2$ and μ_2 $OC\mathit{H}(CH_3)_2$ (ZrZr)), 4.41 (m_{br}, 6H, μ_2 $OC\mathit{H}(CH_3)_2$ (CdZr) and terminal $OC\mathit{H}(CH_3)_2$), 1.55 (d_{br}, 18H, μ_3 $OCH(C\mathit{H}_3)_2$ and μ_2 $OCH(C\mathit{H}_3)_2$ (ZrZr)), 1.32 (d_{br}, 36H, μ_2 $OCH(C\mathit{H}_3)_2$ (CdZr) and terminal $OCH(C\mathit{H}_3)_2$). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6, 298 K; δ/ppm): 128.0 (CdOCN), 71.0 (μ_3 $OCH(CH_3)_2$ and μ_2 $OCH(CH_3)_2$ (CdZr)), 71.8 (μ_2 $OCH(CH_3)_2$ (ZrZr) and terminal $OCH(CH_3)_2$), 26.5 (μ_3 $OCH(CH_3)_2$ and μ_2 $OCH(CH_3)_2$ (CdZr)), 26.8 (μ_2 $OCH(CH_3)_2$ (ZrZr) and terminal $OCH(CH_3)_2$). ^{113}Cd NMR (66 MHz, benzene-d_6, 298 K; δ/ppm): −581. Anal. Found (calcd) for $C_{28}H_{63}CdNO_{10}Zr_2$ (868.65): C, 38.13 (38.72); H, 7.52 (7.31); N, 1.18 (1.61). EI-MS (20 eV; m/z (%)): 821 (8, $[Zr_3(OC_3H_7)_9]^+$), 803 (12, $[Zr_3O(OC_3H_7)_8(OEt)]^+$), 766 (9, $[CdZr_2(OC_3H_7)_8]^+$), 593 (23, $[Zr_3O_3(OC_3H_7)_4(OC_2H_4)_3]^+$), 440 (7, $[Zr_3O_5(OC_2H_4)_2]^+$), 311 (100, $[Zr(OC_3H_7)_3(OC_2H_4)]^+$), 267 (13, $[Zr(OC_3H_7)_3]^+$), 253 (11, $[Zr(OC_3H_7)_2(OC_2H_4)]^+$), 58 (18, $[C_2H_4N]^+$), 45 (100, $[OC_2H_5]^+$).

*Bis(trifluoromethanesulfonato)cadmium Nonaisopropoxydizirconium, $[(\mu\text{-}O_2SOCF_3)Cd\{Zr_2(OPr^i)_9\}]_2$ (**12**).* Educts: $[ICd\{Zr_2(OPr^i)_9\}]$ (0.51 g, 0.53 mmol), $Ag(SO_3CF_3)$ (0.14 g, 0.53 mmol). Yield: 0.49 g (0.5 mmol, 94%) crude product (white solid). ^1H NMR (300.1 MHz, benzene-d_6, 298 K; δ/ppm): 4.67 and 4.57 (overlapping m, 4H, μ_3 $OC\mathit{H}(CH_3)_2$ and μ_2 $OC\mathit{H}(CH_3)_2$ (CdZr)), 4.45 (m, 1H, μ_2 $OC\mathit{H}(CH_3)_2$ (ZrZr)), 4.42 (m, 4H, terminal $OC\mathit{H}(CH_3)_2$), 1.67 (d, 12H, μ_3 $OCH(C\mathit{H}_3)_2$), 1.52 (d, 12H, μ_2 $OCH(C\mathit{H}_3)_2$ (CdZr)), 1.36 (d, 6H, μ_2 $OCH(C\mathit{H}_3)_2$ (ZrZr)), 1.30 (d, 24H, terminal $OCH(C\mathit{H}_3)_2$). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6, 298 K; δ/ppm): 120.5 (SO_3CF_3), 70.1 (μ_3 $OCH(CH_3)_2$), 71.2 (μ_2 $OCH(CH_3)_2$ (CdZr)), 70.6 (μ_2 $OCH(CH_3)_2$ (ZrZr)), 72.1 (terminal $OCH(CH_3)_2$), 26.6 (μ_3 $OCH(CH_3)_2$), 27.6 (μ_2 $OCH(CH_3)_2$ (CdZr)), 26.9 (μ_2 $OCH(CH_3)_2$ (ZrZr)), 27.0 (terminal $OCH(CH_3)_2$). ^{19}F NMR (282.4 MHz, benzene-d_6, 298 K; δ/ppm): −77.1. ^{113}Cd NMR (66 MHz, benzene-d_6, 298 K; δ/ppm): −693. Anal. Found (calcd) for $C_{28}H_{63}CdF_3O_{12}SZr_2$ (975.7): C, 33.93 (34.47); H, 6.85 (6.51); S, 3.64 (3.29). EI-MS (20 eV; m/z (%)): 915 (42, $[SO_3CF_3CdZr_2(OC_3H_7)_7]^+$), 857 (10, $[Zr_3(OC_3H_7)_9O(OC_2H_5)]^+$), 767 (7, $[CdZr_2(OC_3H_7)_8]^+$), 593 (32, $[Zr_3O_3(OC_3H_7)_4(OC_2H_4)_3]^+$), 567 (9, $[Zr_3O_3(OC_3H_7)_2(OC_2H_4)_3]^+$), 440 (15, $[Zr_3O_5(OC_2H_4)_2]^+$), 325 (8, $[Zr(OC_3H_7)_3(OC_3H_6)]^+$), 311 (100, $[Zr(OC_3H_7)_3(OC_2H_4)]^+$), 267 (13, $[Zr(OC_3H_7)_3]^+$), 253 (11, $[Zr(OC_3H_7)_2(OC_2H_4)]^+$), 45 (35, $[OC_2H_5]^+$). Sublimation temperature: 165 °C/10^{-3} mbar.

*Cyanidocadmium Nonaisopropoxydizirconium, $[(NC)Cd\{Zr_2(OPr^i)_9\}]$ (**13**).* Educts: $[ICd\{Zr_2(OPr^i)_9\}]$ (1.68 g, 1.8 mmol), Ag(CN) (0.25 g, 1.8 mmol). Yield: 0.48 g (0.56 mmol, 31.3%) crude product (white solid). ^1H NMR (300.1 MHz, benzene-d_6, 298 K; δ/ppm): 4.80 and 4.69 (m_{br}, 4H, μ_3 $OC\mathit{H}(CH_3)_2$ and $OC\mathit{H}(CH_3)_2$ (CdZr)), 4.64 and 4.59 (m_{br}, 5H, μ_2 $OC\mathit{H}(CH_3)_2$ (ZrZr) and terminal $OC\mathit{H}(CH_3)_2$), 1.70 and 1.90 (d_{br}, 24H, μ_3 $OCH(C\mathit{H}_3)_2$ and μ_2 $OCH(C\mathit{H}_3)_2$ (CdZr)), 1.64 and 1.42 (d_{br}, 30H, μ_2 $OCH(C\mathit{H}_3)_2$ (ZrZr) and terminal $OCH(C\mathit{H}_3)_2$). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6, 298 K; δ/ppm): 149 (CdCN), 69.9 (μ_3 $OCH(CH_3)_2$), 70.6 (μ_2 $OCH(CH_3)_2$ (CdZr)), 70.8 (μ_2 $OCH(CH_3)_2$ (ZrZr)), 71.5 (terminal $OCH(CH_3)_2$), 27.7 (μ_3 $OCH(CH_3)_2$), 26.2 (μ_2 $OCH(CH_3)_2$ (CdZr)), 27.1 (μ_2 $OCH(CH_3)_2$ (ZrZr)), 26.9 (terminal $OCH(CH_3)_2$). ^{113}Cd NMR (66 MHz, benzene-d_6, 298 K; δ/ppm): −603. Anal. Found (calcd) for $C_{28}H_{63}CdNO_9Zr_2$ (852.65): C, 37.33 (39.44); H, 7.31 (7.45); N, 2.16 (1.64). EI-MS (20 eV; m/z (%)): 821 (38, $[Zr_3(OC_3H_7)_9O]^+$), 718 (6, $[Zr_3O_2(OC_3H_7)_7]^+$), 311 (7, $[Zr(OC_3H_7)_3(OC_2H_4)]^+$), 58 (16, $[C_2H_4N]^+$), 45 (100, $[OC_2H_5]^+$).

*Sulfatobis(cadmium nonaisopropoxydizirconium), $[(SO_4)\{Cd\{Zr_2(OPr^i)_9\}\}_2]$ (**14**).* Educts: $[ICd\{Zr_2(OPr^i)_9\}]$ (1.88 g, 2 mmol), $Ag_2(SO_4)$ (0.307 g, 1 mmol). Yield: 2.89 g (1.65 mmol, 82.6%) crude product (yellow solid). ^1H NMR (300.1 MHz, benzene-d_6, 298 K; δ/ppm): 4.88 (m, 2H, μ_3 $OC\mathit{H}(CH_3)_2$), 4.58 and 4.73 (overlapping m, 3H, μ_2 $OC\mathit{H}(CH_3)_2$ (CdZr) and μ_2 $OC\mathit{H}(CH_3)_2$ (ZrZr)), 4.49 (m, 4H, terminal $OC\mathit{H}(CH_3)_2$), 1.73 and 1.77 (overlapping d, 24H, μ_3 $OCH(C\mathit{H}_3)_2$ and μ_2 $OCH(C\mathit{H}_3)_2$ (CdZr)), 1.45 (d, 6H, μ_2 $OCH(C\mathit{H}_3)_2$ (ZrZr)), 1.38 (d, 24H, terminal $OCH(C\mathit{H}_3)_2$). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6, 298 K; δ/ppm): 70.6 (μ_3 $OCH(CH_3)_2$), 70.4 (μ_2 $OCH(CH_3)_2$ (CdZr)), 70.2 (μ_2 $OCH(CH_3)_2$ (ZrZr)), 71.7 (terminal $OCH(CH_3)_2$), 26.4 (μ_3 $OCH(CH_3)_2$), 27.0 (μ_2 $OCH(CH_3)_2$ (CdZr)), 26.6 (μ_2 $OCH(CH_3)_2$ (ZrZr)), 26.8 (terminal $OCH(CH_3)_2$). ^{113}Cd NMR (66 MHz, benzene-d_6, 298 K; δ/ppm): −624. Anal. Found (calcd) for $C_{54}H_{126}Cd_2O_{22}SZr_4$ (1749.33): C, 37.2 (37.08); H, 7.7 (7.26); S, 0.8 (1.83). EI-MS (20 eV; m/z (%)): 821 (88, $[Zr_3(OC_3H_7)_9O]^+$), 719 (8, $[Zr_3O_2(OC_3H_7)_7]^+$), 593 (9, $[Zr_3O_3(OC_3H_7)_4(OC_2H_4)_3]^+$), 567 (8, $[Zr_3O_3(OC_3H_7)_2(OC_2H_4)_3]^+$), 311 (7, $[Zr(OC_3H_7)_3(OC_2H_4)]^+$), 58 (32, $[C_2H_4N]^+$), 45 (100, $[OC_2H_5]^+$).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, tables, and CIF files giving X-ray crystallographic data and additional analytical data (^1H NMR spectra, DTA curves and molecular structures) of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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