

Main Group Catalysis

A Highly Lewis Acidic Strontium *ansa*-Arene Complex for Lewis Acid Catalysis and Isobutylene Polymerization

Philipp Dabringhaus, Marcel Schorpp, Harald Scherer, and Ingo Krossing*

Abstract: The potential of a dicationic strontium *ansa*-arene complex for Lewis acid catalysis has been explored. The key to its synthesis was a simple salt metathesis from SrI_2 and $2Ag[Al(OR^F)_4]$, giving the base-free strontium-perfluoroalkoxyaluminate $Sr[Al(OR^F)_4]_2$ ($OR^F = OC(CF_3)_3$). Addition of an *ansa*-arene yielded the highly Lewis acidic, dicationic strontium *ansa*-arene complex. In preliminary experiments, the complex was successfully applied as a catalyst in CO_2 -reduction to CH_4 and a surprisingly controlled isobutylene polymerization reaction.

Lewis acidity plays a decisive role in modern main group catalysis. In the last decade, frustrated Lewis pairs (FLPs) have emerged as flagship of main group catalysis.^[1] The reactivity of FLPs originates from the synergistic reactivity of a Lewis acid and Lewis base, which are sterically hindered from a quantitative adduct formation.^[2] The most widely used Lewis acid for FLP catalysts represents the soft Lewis superacid $B(C_6F_5)_3$.^[3] Yet, recent reports suggest the importance of more pronounced hard Lewis acids to broaden the scope of FLP catalysts and enhance their activity, for example, for CO_2 activation.^[4] Exceptionally strong p-block Lewis acids, for example, $Al(C_6F_5)_3$, have been shown to effectively catalyze FLP-type hydrosilylations of 1-olefins,^[5] CO_2 reduction,^[6] and FLP-polymerizations.^[7] Similarly to FLPs, the emerging class of alkaline earth metal catalysts of the type L-M-R (L = innocent ligand) depend on the cooperative electrophilicity of the metal atom (M) and the nucleophilicity of the reactive, anionic ligand (R), for example, a hydride or formal carbanion. In recent years, Harder and Hill impressively reinvented the field of organometallic alkaline earth (Ae) metal catalysis.^[8,9] Ae catalysis evolved around σ -bond metathesis and polarized insertion as principal mechanistic steps. Substrate activation via coordination to the metal is widely accepted to critically rely on the Ae metal's Lewis acidity.^[10] Yet, the Lewis acidity of common Ae complexes is limited by the need for kinetic stabilization of the extremely

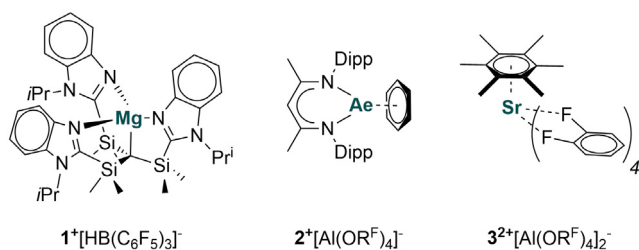
reactive “naked” Ae^{2+} cations by large, anionic ligands, for example, encumbered beta-diketiminato ligands (NacNac). This represents a significant drawback compared to FLP catalysts with strong p-block acids. Hence, the opening of the field of Ae catalysis to FLP-type chemistry demands for the development of Ae salts with highly Lewis acidic, cationic Ae moieties. In the literature, FLP systems incorporating Ae metals are scarce. In 2017, the group of Harder used a Mg-based Lewis acid of type $(NacNacMgBr)_2$ in combination with PPh_3 for substrate activation of polar substrates, for example, acetone.^[11] Moreover, the same group published a Ca^{II}/Al^I -FLP for stoichiometric benzene reduction, which heavily relied on the substantial reactivity of the Al^I species.^[12] Although the overall neutral complexes including Ae^{2+} ions are significantly less Lewis acidic than neutral Al^{3+} or B^{3+} based compounds, the Lewis acidity can be enhanced by synthesis of cationic Ae^{2+} complexes as salts of weakly coordinating anions (WCAs). Recently, Okuda demonstrated for such a mono-cationic calcium hydride complex bound to a neutral tetraamine ligand the increase of catalytic activity.^[13] As a first example for a cationic Ae-based Lewis acid catalyst, Parkin reported the cationic Mg-complex **1**^[14] stabilized with a bulky tetradentate ligand to prevent coordination of the hydridic counter ion $[HB(C_6F_5)_3]^-$ ^[15] as catalyst for an FLP-type hydrosilylation of CO_2 . Harder and Hill independently developed several complex salts of the type $[Ae(NacNac)]^+ [WCA]^-$ ($[WCA]^- = [B(C_6F_5)_4]^-$, $[Al(OR^F)_4]^-$ with $OR^F = C(CF_3)_3$; Ae = Mg, Ca).^[16,17] Their pronounced Lewis acidity was unambiguously shown by isolation of the respective metal-arene complexes upon addition of benzene (**2**⁺), toluene, *m*-xylene and mesitylene.^[18] Inspired by the surprisingly persistent coordination between the hard Ae^{2+} ions and soft arenes, our group reported a first synthesis of unsupported, dicationic alkaline earth metal arene complexes via oxidation of the Ae metals (Ae = Ca, Sr (**3**²⁺), Ba) with the hexamethylbenzene-radical cation salt $[HMB][al-f-al]$ as oxidant ($[al-f-al]^- = [(^FRO)_3Al-F-Al(OR^F)_3]^-$).^[19] On the basis of the computed fluoride-ion affinities (FIA) of **3**²⁺ in CH_2Cl_2 solution, Lewis acidities similar to the hard acids $Al(C_6F_5)_3$ or $Al(OR^F)_3$ were derived for the Ae^{2+} complexes making them promising Lewis acid catalysts. Unfortunately, the fleeting stability of these salts, in particular the Ca and Ba variants, as well as inseparable radical impurities encumbered the application of these salts in catalysis.

With the aim to develop an improved synthetic route towards highly pure dicationic Ae complexes with neutral ligands, we investigated the salt metathesis between $Ag[Al(OR^F)_4]$ and excess SrI_2 in 1,2-difluorobenzene (*o*-DFB) promoted by ultrasonic irradiation as in Equation (1).

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Here, the solvent-free crystalline $\text{Sr}[\text{Al}(\text{OR}^{\text{F}})_4]_2$ **4** was isolated in a high yield of 92%. The bulk purity of **4** was confirmed by X-ray powder diffraction (Supporting Information, Figure S7).



The molecular structure of **4** reveals an extraordinary $\kappa^3\text{-O,O',O''}$ -coordination of the cation to one of the anions, which induces an elongation of the respective Al–O bonds to $d_{\text{Al-O,avg.}} = 1.772(4)$ Å and short Sr–O distances of $d_{\text{Sr-O,avg.}} = 2.655(5)$ Å (Figure 1). Overall, the best formulation describing the composition of **4** and considering the structure would be $[\text{Sr}\{\text{Al}(\text{OR}^{\text{F}})_4\}]^+[\text{Al}(\text{OR}^{\text{F}})_4]^-$. The second anion in **4** is weakly coordinated to $[\text{Sr}\{\text{Al}(\text{OR}^{\text{F}})_4\}]^+$ over three fluorine atoms. In the IR spectrum, this κ^3 -coordination induced band splitting of degenerate modes, due to the reduction of the typical S_4 -symmetry of the free anion, for example, in the undistorted salt $[\text{NEt}_4]^+[\text{Al}(\text{OR}^{\text{F}})_4]^-$.^[20] A CCDC search revealed, only cation- $\kappa^2\text{-O,O'}$ -coordination to $[\text{Al}(\text{OR}^{\text{F}})_4]^-$ was previously reported.^[21] Negligible contamination by the dimeric compound $[\text{Sr}_2(\mu\text{OR}^{\text{F}})_2(\text{o-dfb})_6]^{2+}([\text{Al}(\text{OR}^{\text{F}})_4]^-)_2$ was observed by single crystal X-ray analysis (Figure S8). The high Lewis acidity of the strontium atom, already visible from the unusual tripod anion coordination, is further underlined by coordination of trace acetone and water—present in the

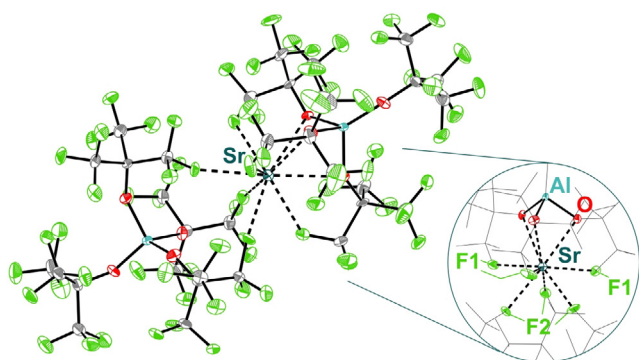
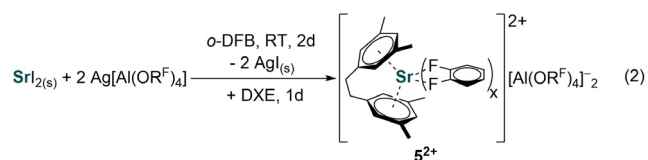


Figure 1. Molecular structure of $\text{Sr}[\text{Al}(\text{OR}^{\text{F}})_4]_2$. Thermal displacement of the ellipsoids was set at 50% probability. Selected interatomic distances for **4** in Å given as ranges and averages due to multiple molecules in the asymmetric unit: Al–O_{range} = 1.763(6)–1.787(6), Al–O_{avg.} = 1.772(4), Sr–O_{range} = 2.620(5)–2.681(5), Sr–O_{avg.} = 2.655(5), Sr–F1_{range} = 2.519(6)–2.578(6), Sr–F1_{avg.} = 2.551, Sr–F2_{range} = 2.514(5)–2.653(5), Sr–F2_{avg.} = 2.568(5).

mass spectrometer as impurities—to the generated $[\text{Sr}\{\text{Al}(\text{OR}^{\text{F}})_4\}]^+$ cation (Figure S11). Yet, the narrow peak widths of the ^{19}F and ^{27}Al NMR resonances (^{19}F NMR: $\Delta\omega_{1/2} = 2.2$ Hz, ^{27}Al NMR: $\Delta\omega_{1/2} = 22.9$ Hz; Figures S5 and S6) indicate that the anions are presumably quantitatively exchanged for solvent molecules in *o*-DFB solution. Hence, **4** is anticipated to in situ generate a highly reactive, *o*-DFB solvated strontium dication, which can be trapped by neutral Lewis bases with a stronger coordination ability than *o*-DFB.

Arenes represent a promising ligand class due their tunability and soft Lewis basicity allowing for access to highly Lewis acidic Ae complexes with an open coordination sphere compared to ligands commonly used in Ae complexation chemistry. Chelating *ansa*-arenes—related to the *ansa*-metallocenes—would add entropic stability to the corresponding complexes and allow for an empty coordination space opposite to the *ansa*-bridge. Hence, to probe the synthetic potential of the salt metathesis, dixylyethylene (DXE) was added to **4**, prepared as an intermediate in the reaction of SrI_2 and $\text{Ag}[\text{Al}(\text{OR}^{\text{F}})_4]$ as in Equation (2). The molecular structure of the isolated (in 96% yield) Ae *ansa*-arene complex **5** is displayed in Figure 2. The high bulk purity of **5** was confirmed by powder X-ray diffraction (Figure S20).



In the molecular structure, the metal cation is in addition to the DXE ligand coordinated by two κ^2 -bound *o*-DFB molecules with Sr–F distances between 2.534(2) Å and 2.669(2) Å (Figure 2).^[19,22] Moreover, both aromatic rings adopt an η^6 -coordination with Sr–C distances ranging from 2.945(3)–3.117(3) Å. These values coincide with previously reported distances for the strontium HMB complex.^[19]

The cation-arene interaction was analyzed by means of the quantum theory of atom in molecules (QTAIM). The calculated electronic charge densities ρ and Laplacians of the

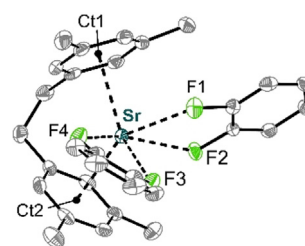


Figure 2. Molecular structure of the dicationic moiety in $[\text{Sr}(\text{DXE})-(\text{o-DFB})_2]^{2+}([\text{Al}(\text{OR}^{\text{F}})_4]^-)_2$ **5**. Thermal displacement of ellipsoids set at 50% probability. Protons and counterions were omitted for clarity. Selected interatomic distances for **5**²⁺ in Å given as ranges and averages due to multiple cationic moieties in the asymmetric unit: Sr–{F1/F3}_{range} = 2.636(2)–2.669(2), Sr–{F1/F3}_{avg.} = 2.651(2), Sr–{F2/F4}_{range} = 2.534(2)–2.559(2), Sr–{F2/F4}_{avg.} = 2.541(2), Sr–C[Ar]_{range} = 2.945(3)–3.117(3), Sr–C[Ar]_{avg.} = 3.008(3), Sr–{Ct1/Ct2}_{range} = 2.655–2.681, Sr–{Ct1/Ct2}_{avg.} = 2.667.

electron density $\Delta\rho$ are summarized along with results of QTAIM and natural bond orbital (NBO) population analyses in Figure 3a. In analogy to QTAIM studies on known Ae arene complexes,^[16,19] the partial positive charge on the arene ligand indicates a ligand-to-metal bonding. Computed electron densities at the cage and bond critical points (CCP & BCP) match ρ values obtained for the strontium HMB complex 3^{2+} .^[19] This implies an interaction energy per arene moiety of DXE comparable to HMB. The positive Laplacian of electron density $\nabla\rho$ at the BCPs and CCPs illustrates the depletion of electron density in the interatomic surface, strongly indicating non-covalent interactions. In contrast, covalent cation-arene interactions, for example, in a proton-benzene complex, are characterized by a negative Laplacian.^[23] Nonetheless, calculated bonding MOs unambiguously display an interaction of strontium *d*-orbitals with the π -system of both arene moieties as a ligand-(π)-to-metal-(*d*) bonding (Figure 3b).^[24] Hence, a covalent contribution to the predominantly ionic bonding can be assumed.

To evaluate the Lewis acidity of **5**, the fluoride and hydride ion affinities (FIA/HIA) were calculated in the gas phase and in the condensed phase in dichloromethane DCM ($\epsilon(\text{DCM}) = 9.08$ ^[25]). The DCM-values were shown to successfully level the influence of the charges upon comparing Lewis acidities.^[26,27] FIA and HIA values were referenced to SiMe_3^+ calculated at the CCDS(T)/CBS^[27] level and G3 level^[28] respectively (Table 1). As desired by enhancing the soft-hard mismatch interaction with the chelating *ansa*-arene ligand, **5** reaches an even higher FIA value than the known strontium HMB complex in gas phase and condensed phase. Although DCM-solvation of the cation leads to significant

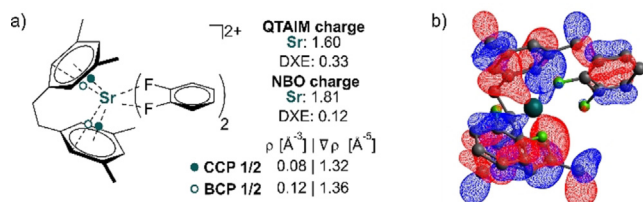


Figure 3. a) Population analyses by QTAIM and NBO as well as electron densities and Laplacian at bond and cluster critical points. b) HOMO-6 of the optimized structure of 5^{2+} (BP86/D3(BJ)/def-SVP).

Table 1: Summary of calculated XIA values for various Ae complexes and example p-block Lewis acids (BP86/D3(BJ)/def2-SVP/CPCM; $\epsilon(\text{DCM}) = 9.08$ ^[25]).

| Lewis acid | FIA _{Gas} | FIA _{DCM} | HIA _{Gas} | HIA _{DCM} |
|--|--------------------|--------------------|--------------------|--------------------|
| SbF ₅ | 484 | 303 | — ^[a] | — |
| Al(C ₆ F ₅) ₃ | 548 | 308 | 494 | 178 |
| Al(OR ^F) ₃ | 544 | 316 | 491 | 187 |
| B(C ₆ F ₅) ₃ | 458 | 232 | 488 | 182 |
| [Sr(DXE)(κ^2 - <i>o</i> -DFB) ₂] ²⁺ | 935 | 274 | 827 | 104 |
| [Sr(<i>o</i> -DFB) ₂] ²⁺ ^[b] | 871 | 232 | 751 | 56 |
| [Sr(HMB)(κ^2 - <i>o</i> -DFB) ₄] ²⁺ | 867 | 240 | 753 | 66 |
| [Sr(NacNac)] ⁺ | 699 | 233 | 593 | 71 |

[a] [SbF₅H][−] is unstable^[28] and thus the HIAs were omitted.

[b] [Sr(*o*-DFB)₂]²⁺ is the DFT calculated optimum structure of Sr²⁺ only solvated by *o*-DFB (Supporting Information).

dampening of the FIA, **5** is expected to retain a similar Lewis acidity to strong p-block Lewis acids (Table 1).

Since **5** was intended to be used as homogenous catalyst, it is crucial that the *ansa*-arene coordination to the metal is retained in solution. The comparison of ¹H,¹³C HMBC spectra of the free ligand and the strontium-DXE complex, both measured in *o*-DFB, reveal only a shift of the resonances assigned to the aromatic carbon atoms of $\Delta\delta^{13}\text{C} = 0.56$ –1.56 ppm. For comparison, in the complex 3^{2+} a downfield shift of $\Delta\delta^{13}\text{C} = 2.4$ ppm was reported for the aromatic carbon atoms upon coordination to the metal.^[19] In addition, NMR analysis revealed only a slight dampening of the diffusion constant of DXE in a solution of **5** in *o*-DFB compared to free DXE (Supporting Information, Tables S1 and S2). This observation indicates that the majority of the ligand is displaced by *o*-DFB molecules. Therefore, we switched the solvent *o*-DFB for 1,2,3,4-tetrafluorobenzene (TFB). TFB possesses a considerably diminished coordinating ability (Figure 4a), owing to the lower negative partial charge per fluorine atom, whereas the polarity and the physical properties closely resemble those of *o*-DFB (see ref. [29] and Table S12). As anticipated, a significant shift of proton and carbon resonances is observed for **5** compared to the free ligand in TFB solution (Figure 4b). In combination with a pronounced peak broadening of the proton signals in the ¹H NMR spectrum (Figure S16), the NMR spectra indicate coordination of the *ansa*-arene to the electron withdrawing strontium ion in TFB solution. These observations are supported by a significant dampening of diffusion constants determined by means of NMR spectroscopy (Tables S1 and S2). The ²⁷Al NMR resonance attributed to the [Al(OR^F)₄][−] anion is strongly broadened in TFB ($\Delta\omega_{1/2} = 617$ Hz, Figure S18), whereas the respective signal in *o*-DFB is sharp ($\Delta\omega_{1/2} = 29$ Hz, Figure S14) and comparable to free [Al(OR^F)₄][−] in [NET₄]⁺[Al(OR^F)₄][−] ($\Delta\omega_{1/2} = 12$ Hz).^[20]

Hence, although NMR-spectroscopic analysis reveals the dissociation of DXE from **5** in *o*-DFB, the analysis for **5** in TFB strongly indicates coordination of the DXE ligand as well as a stronger interaction of the strontium ion to the anion.

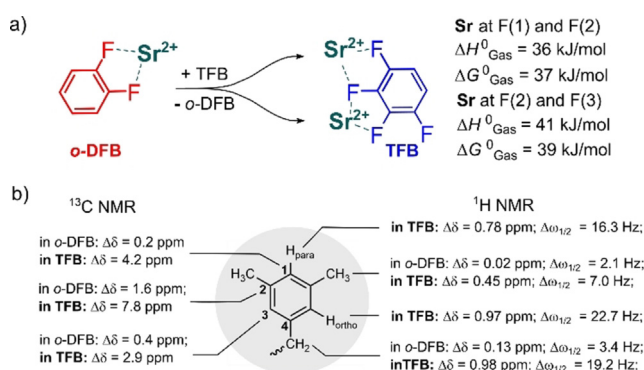


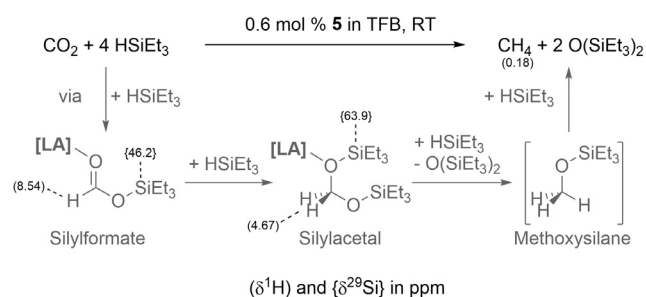
Figure 4. a) Endothermic and endergonic calculated thermodynamics of the isodesmic solvent exchange reactions at [Sr(*o*-DFB)]²⁺ with TFB yielding two isomers of [Sr(TFB)]²⁺ (BP86-D3(BJ)/def-SVP). b) Comparison of the chemical shift differences and peak widths observed in ¹H NMR spectra of **5** and free dixylyethylene in *o*-DFB and TFB.

To study the reactivity of the highly Lewis acidic strontium *ansa*-arene complex preliminarily, **5** was applied as catalyst in FLP-type catalysis typically achieved with strong p-block Lewis acids. Here, the results of the solution structure studies on **5** were confirmed experimentally by altering its reactivity, since **5** was found unreactive for catalysis in *o*-DFB-solution. Thus, subsequent reactions were exclusively performed in TFB.

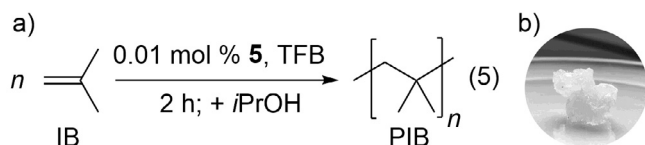
In a first catalytic transformation, only 0.6 mol% **5** successfully catalyzed the reduction of CO₂ straight to methane with triethylsilane as hydrogen source (Scheme 1). Previously, Lewis acid catalyzed hydrosilylations of CO₂ to CH₄ have only been reported for a synergistic catalyst comprised of Al(C₆F₅)₃/B(C₆F₅)₆^[6] and for salts with the highly Lewis acidic, cationic [AlR₂]⁺ moiety (R = Et,^[30] OAr^[31]). A high selectivity for CH₄ was observed (23% respective to silane) by monitoring the reaction with NMR spectroscopy, whereas only diminished amounts of the intermittently generated silylformate and silylacetal complexes were detected (Supporting Information). Unfortunately, the reduction was rather slow, thus, only 24% of initially used silane have reacted after 14 d. Nonetheless, the successful hydrosilylation of thermodynamically highly stable CO₂ clearly demonstrates the catalytic potential of dicationic Ae-arene complexes.

Moreover, **5** was tested as initiator for the cationic polymerization of highly reactive isobutylene at –12 °C and 0 °C (Scheme 2a). Only 0.01 mol% **5** was sufficient and polymers were isolated as viscous, rubber-like materials (Scheme 2b).

In contrast, common catalysts at similar conditions yield oily, low-molecular weight polyisobutylenes ($M_w < 2000 \text{ g mol}^{-1}$), whereas medium-to-high molecular weights



Scheme 1. Postulated pathway for stepwise hydrosilylation of CO₂ to CH₄. Lewis acid adducts (indicated by [LA]) of silylformate and silylacetal were observed by NMR spectroscopy and the chemical shifts are given (Supporting Information). Formation of methoxysilane is hypothetical as it could not be detected in the NMR experiment.



Scheme 2. a) Polymerization of 2.0–2.3 g isobutylene initiated by 0.01 mol% **5** in 1,2,3,4-tetrafluorobenzene (10 mL). Initiator concentration refers to amount of isobutylene used. b) Picture of rubber-like polyisobutylene isolated in polymerization at –12 °C.

($M_w > 1 \times 10^5 \text{ g mol}^{-1}$) and narrow dispersities ($D < 2.0$) are typically only achieved at temperatures below –80 °C.^[32] Excitingly, the polymer isolated from the –12 °C polymerizations in TFB revealed in GPC analyses a high molecular weight of $M_w = 1.30 \times 10^5 \text{ g mol}^{-1}$ in combination with a narrow molecular mass distribution ($D = 1.87$)—similar to the current record holding scandium catalysts.^[33] These results coincide with the strong analogy in reactivity between lanthanides and alkaline earth metals.^[8] Recently, various cationic rare earth metal complexes have been reported to allow for a surprisingly controlled polymerization of isobutylene, yielding medium-to-high molecular weight polyisobutylene ($M_w > 1 \times 10^5 \text{ g mol}^{-1}$) with low dispersities ($D = 1.8$) at elevated temperatures up to –15 °C.^[33,34] In accordance with the typical characteristics of cationic polymerizations, a higher reaction temperature of 0 °C resulted in our case to a lower molecular weight of the isolated polymers ($M_w = 0.70 \times 10^5 \text{ g mol}^{-1}$).

In summary, we reported on the isolation of the solvent-free strontium complex Sr[Al(OR^F)₄]₂ with an unprecedented tripodal coordination of one of the [Al(OR^F)₄][–] anions. Due to the weakly coordinating character of the anion, the WCAs can be easily replaced by weak, neutral ligands, thereby opening a simple route towards highly Lewis acidic, dicationic alkaline earth metal complexes. As a first example, the synthesis of a strontium *ansa*-arene complex **5** was presented. The catalytic activities of highly Lewis acidic **5** in hydrosilylation of the thermodynamically extremely stable molecule CO₂ represent promising studies for broadening the scope of alkaline earth metal catalysis to FLP-type reactions typically achieved with strong p-block Lewis acids such as Al(C₆F₅)₃ or B(C₆F₅)₆. Moreover, **5** was able to initiate a remarkably controlled polymerization of isobutylene at elevated temperatures.

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Conflict of interest

The authors declare no conflict of interest.

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