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Dedication to Prof. Werner Uhl on the Occasion of his 65th Birthday

Abstract. Cp_3Ln (Ln = Ce, Nd, Sm, Er, Yb) are applied as precatalysts in the presence of LiAlH₄ for the C–F bond activation of hexafluoropropene, 1,1,3,3,3-pentafluoropropene, trifluoropropene, chlorotrifluoroethene, and octafluorotoluene. 100% conversion and TONs up to 155 could be observed for the hydrodefluorination reaction (HDF). For chlorotrifluoroethene hydrodefluorination occurs with high chemoselectivity favoring the C–F bond activation versus C–Cl bond activation.

Introduction

Complexes of the rare earth metals find widespread application as catalysts in polymerization,^[1] hydrogenation,^[2] hydrosilylation,^[3] hydroamination,^[2a,4] and hydroboration^[2a,5] reactions. Lanthanide compounds are hard Lewis acids and their most stable oxidation state is +III. With fluorine they form strong bonds (BDE approx. 500–670 kJ·mol⁻¹; except Lu: 404 kJ·mol⁻¹),^[6] making them suitable for C–F bond activation reactions. Organofluorine compounds found a broad field of application in the chemical industry (pharmaceuticals, polymers, coatings, refrigerants).^[7] However, a drawback of the high thermodynamic stability and kinetic inertness of the C–F bond is the accumulation of fluorocarbons in the upper atmosphere where they contribute to the global warming effect.^[8] Therefore, it is of great interest to selectively construct and deconstruct C–F bonds.

Next to the well-investigated transition metal mediated C–F bond activation,^[9] the rare earth metals promise great opportunities and novel reactivity. Lanthanides show significant intramolecular interactions with C–F bonds, which results in a relatively low activation barrier for C–F activation.^[10] In 1994 *Deacon* reported some evidence for catalytic C–F bond activation with an organoytterbium reagent by addition of a cyclopentadiene source.^[11] However, except of that, so far all reported C–F bond activations mediated by lanthanide complexes are stoichiometric reactions and no catalytic systems are known.^[12] The first lanthanide mediated C–F bond activation was accomplished by *Deacon* with metallic samarium and bis(pentafluorophenyl)mercury in a complex redox transmetallation reaction.^[13] *Andersen* and *Watson* showed that divalent lanthanide complexes abstract fluorine atoms from per-

fluoroolefins and hexafluorobenzene.^[14] *Brennan* reported the formation of SmF₃ by decomposition of a dimeric samarium(III) complex with fluorinated benzenethiolate ligands.^[15] Experimental and computational studies on the C–F activation with monomeric Cp'₂CeH and Cp'₂CeCH₂Ph [Cp' = 1,2,4-(Me₃C)₃C₅H₂] were conducted by *Maron*, *Eisenstein*, and *Andersen*.^[16] These studies showed that for the reactions with Cp'₂CeH intermolecular C–H activation proceeds with a lower barrier than C–F activation, which is the rate-determining step.

In 2015 *Deacon* and *Junk* disclosed that a lanthanum formamidinate complex undergoes C–F activation of all fluorine atoms of one CF_3 group to produce LaF_3 and two different poly(trifluorophenyl)amidines, which provides a new synthetic method in the preparation of functionalized amidines.^[17]

Our aim was to find a catalytic system based on rare earth metal complexes for the activation of the C-F bond. Among the tested systems the divalent samarium complex $Cp*_2Sm(THF)_2$ ($Cp* = C_5Me_5$) turned out to be the most effective precatalyst for hydrodefluorination reactions with Group 13 hydrides as hydride source (see Supporting Information). However, in control experiments we found out that for the HDF of several fluoroorganic compounds with alkylaluminum hydrides as hydride sources in toluene no metal complex is needed just catalytic amounts of donor solvents.^[18] In conclusion, the catalytic activity of Cp*₂Sm(THF)₂ may be derive from the coordinated THF molecules and not from the central metal atom. Therefore, we applied several tris(cyclopentadienyl) rare earth metal complexes Cp_3Ln [Ln = Ce (1a), Nd (1b), Sm (1c), Er (1d), Yb (1e)], which we obtained from a commercial supplier, who claimed that the elemental analysis shows no THF, to exclude interference of possible organocatalytic HDF. Nonetheless, to be sure that no THF is present, we measured a ¹H NMR spectrum of Cp₃Yb (1e), which is consistent with literature data^[19] for non-coordinated 1e and shows no signals of THF. The rare earth metals qualify for reactivity studies because their cations form a group with gradual contraction of the ionic radii but constant ionic charge. Therefore, we choose five rare earth metals (Ce, Nd, Sm, Er, Yb) distributed over the whole group.

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Generating C-H bonds and regeneration of the catalyst requires a hydride source (E-H). The driving force for catalyst regeneration in HDF reactions can be the formation of strong element fluorine bonds (E-F). Silicon, boron, aluminum, and gallium show high bond dissociation energies (BDE) towards fluorine and their E-F bonds are stronger than most metal fluoride bonds.^[6] Their hydrides are possible candidates as hydride sources in catalytic HDF reactions. Several studies demonstrated the hydrogen transfer capability of e.g. phenylsilane^[20] and alkylalanes^[21] with alkyl and carboxylate complexes of the rare earth metals. Furthermore, Rosenthal et al. demonstrated that zirconium fluorido complexes were converted into the corresponding hydrido complexes by diisobutylaluminum hydride (DIBAL).^[22] C-F bond activation by LiAlH₄ in ether is long known,^[23] but catalytic systems are rare and based on transition metal salts.^[24]

Results and Discussion

The system with diisobutylaluminum hydride (4a) as hydride source and Cp₃Yb (1e) as precatalyst showed no reactivity towards the HDF of hexafluoropropene (6) (see Supporting Information). Therefore, we applied lithium aluminum hydride (4b) as hydride source for the HDF of 6 (Table 1). Quantitative conversion to the HDF products could be observed. In addition to the main products 7a and 7b, 2nd generation HDF products *E*- and *Z*-1,2,3,3-tetrafluoropropene (7d-7e) were obtained as minor products (10-24%). The other constitutional isomer 1,1,2,3,3-pentafluoropropene (7c), 2nd generation HDF product 2,3,3,3-tetrafluoropropene (8a) and 3rd generation HDF product 2,3,3-trifluoropropene (9b) could be obtained in small amounts. Interestingly, the E/Z ratio is above 1 for all precatalysts; i.e. the thermodynamically less stable E-isomer is prevailingly formed. The E/Z ratio of the 2nd generation HDF products 7e and 7d is below 1; the Z isomer is favored. The most reactive system for the HDF of 6 is the system using 1e as precatalyst (entry 5); quantitative conversion to the HDF products and a higher selectivity than for the reactions with the other prectalysts was observed. When the amount of precatalyst **1e** was reduced to just 0.5 mol%, the conversion decreased to 73% (entry 5a). However, the TON increased to 155. The HDF reactions are rather slow: after 1 h reaction time just 0.3–8.5% conversion to the HDF products could be observed (see Supporting Information).

To study the limitations and scope of the rare earth metal catalyzed HDF, the best systems using **1a–1c**, **1e** as precatalyst were applied to other olefinic and aromatic substrates as presented in Table 2. Whereas the reactivity of **1e** was high for the HDF of **6**, the conversions for the other substrates are by far lower for **1e** in comparison to the other precatalysts **1a–1c**, i.e. the rare earth metals with larger ionic radii show now higher reactivity.

The main product of the HDF of 1,1,3,3,3-pentafluoropropene (**7f**) is the thermodynamically more stable *E* isomer of 1,3,3,3,-tetrafluoropropene (**8b**) with high *E/Z* ratios up to 9.8 and conversion up to 88% for **1c** (entry 2). The HDF of **11** gives in high selectivity the thermodynamically less stable *E* isomer of 1,2-difluoroethene (**12a**) with *E/Z* ratios around 11. The best system is LiAlH₄ with precatalyst **1b** yielding 78% conversion to the HDF products (entry 6), closely followed by the system with **1a** (entry 5). The systems with LiAlH₄ and precatalysts **1c** and **1e** show low conversions around 28% (entry 7, 8).

To study the competition between hydrodefluorination and other hydrodehalogenation reactions chlorotrifluoroethene (13) was used as substrate (entry 9–12). Surprisingly, the main products are the *E* and *Z* isomer of the chlorinated difluoro ethene. Hence, the C–F activation is preferred over the C–Cl bond activation although the BDE of the C–Cl bond $(370 \text{ kJ} \cdot \text{mol}^{-1})$ is significantly smaller than for the C–F bond $(500 \text{ kJ} \cdot \text{mol}^{-1})$.^[6] The same applies for the BDE of the Sm–X and Al–X bonds (see Supporting Information). The reactions show a relatively high chemoselectivity. However, the regio-

Table 1. HDF of 6 with precatalyst 1a-1e and LiAlH₄ as hydride source in toluene at 80 °C, overnight ^{a)}.

	F	CF ₃ F F F 6 5 mol% 1a 1.5 eq. LiA toluene 80 °C, 20	$ \begin{array}{c} \stackrel{-\mathbf{e}}{\stackrel{IH_4}{\longrightarrow}} & \stackrel{CF_3}{\stackrel{F}{\longrightarrow}} & \stackrel{F}{\stackrel{F}{\longrightarrow}} \\ h & \stackrel{F}{\stackrel{F}{\longrightarrow}} \end{array} $	CF ₂ H F F +	F ^{CF₂H} F ⁷ F ⁷	F ^{CF3}	^{CF} ₂ H		
			main products	traces	minor products	tra	aces		
Entry	Precat.	7a,7b /%	<i>E/Z</i> 7a,7b	7d,7e /%	<i>E</i> / <i>Z</i> 7d	l, 7e	Conv. b) /%	TON	
1	1a	71.1	1.6	21.6	0.29		96.9	24.2	
2	1b	69.5	1.6	23.9	0.24		97.1	24.8	
3	1c	74.8	1.7	10.4	0.33		88.4	20.2	
4	1d	31.9	1.5	4.7	0.24		39.9	9.2	
5	1e	81.9	2.0	14.7	0.30		100	23.6	
5a ^{c)}	1e	64.7	1.6	6.2	0.27		72.5	155	

a) Reaction conditions: 5 mol% precatalyst $Cp_3Ln [Ln = Ce (1a), Nd (1b), Sm (1c), Er (1d), Yb (1e)], 1.5 equiv. LiAlH_4, 1 mmol 6 in toluene at 80 °C, overnight. b) Total conversion; Conversions were determined by ¹⁹F NMR spectra by integration of product resonances vs. the internal standard (fluorobenzene); full Table in Supporting Information. c) 0.5 mol% 1e. d) Mixtures of fluorocarbons and alanes or LiAlH_4 are thermodynamically unstable and can lead to explosions.$ **CAUTION**is required especially in regard to scale up.

SHORT COMMUNICATION

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Entry	Substrate	Precat.	Mol%	Time /h	Main produc	ts /%			E/Z	Conv. 1%	TON
	CF ₃ F				CF ₃	CF ₃	CF ₃	CH₃			
	7f				8b	8c	9a	10b			
1		1a	5.7	17	66.9	9.3	1.7	1.4	7.2	79.9	15.4
2		1b 10	6.3 5.6	17	73.6	7.5	2.5	2.3	9.8	87.6 86 7	15.8
4		1e	5.8	17	22.1	2.8	0.1	2.9 ^{b)}	9.0 7.9	27.9	4.8
	F F				,F	F F	F	F			
	11				12a	12b	12c	12d			
5		1a	4.7	67	67.3	5.7	1.3	0.2	11.9	74.5	16.3
6 7		1b 1c	4.8	67 69	69.9 22.4	6.2 2.3	1.3	0.2	11.2	77.6 28.6	16.4 6.3
8		1e	4.5	67	24.0	2.3	0.4	0.1	11.6	26.7	6.0
	CI		·		CI	CI	Ę	E			
	F F				ک س ے F F	رر F	F	_/			
	13				14a,14b	14c,14d	12a,12b	12c			
9		1a	5.1	21	22.1	4.0	1.9	-	1.0 e)	28.0	6.6
10 11		10 1c	5.1 5.0	18 17	18.0	2.7	1.2	0.1 0.4 c)	$1.0^{(e)}$	22.0	5.0 7.0
12		1e	4.9	17	2.4	0.7	0.7	-	1.0 ^{e)}	3.8	1.1
	CF3				CE		CF3				
	F F		F F		F						
	F	F			F		F	F			
	15				16a		16b				
13		1a	4.7	17	11.1		1.1			12.2	2.6
14 15		1b 1c	4.8 4.8	18 17	9.1 11.0		0.8			10.0	2.1
16		1e	4.8	17	2.6		0.6			3.2	0.7

Table 2. Catalytic HDF of various substrates with precatalyst 1a-1c, 1e, and LiAlH₄ (4b) ^{a)}.

a) Reaction conditions: 5–6 mol% precatalyst **1a–1c**, **1e**, 1.5 equiv. LiAlH₄ in toluene at 80 °C. b) Conversion to 1,1,3,3-tetrafluoropropene (**8d**). c) Conversion to trifluoroethene (**11**). d) The amount of the conversion is the sum of all HDF products (major, minor and all traces) and therefore may differ from the sum of the main products. [e] E/Z ratio of **14a**,**14b**; full Tables see Supporting Information.

selectivity of the HDF of 13 is rather low and conversions of max. 30% (entry 11) could be observed.

The conversions for the HDF of octafluorotoluene (15) are low (up to 12%, entry 15). The main product is the *para*-substituted HDF product heptafluorotoluene (16a).

The equimolar reaction of **1e** with **6** (in toluene, 80 °C, overnight, no color change of the reaction mixture) yields no defluorinated products of **6** but just the recovery of **6**, i.e. no fluorine abstraction or exchange takes place. However, when **1e** is reacted with LiAlH₄ the reaction mixture changes from green to yellow. Unfortunately, the solubility in toluene is very poor and no product signals could be detected in the NMR spectra of the supernatant solution. When the residue is taken up in [D]THF the color changes to red-brown. The ¹H NMR spectrum shows four very broad signals (5.7, 2.9, -15.7, -43.4 ppm), which could not be assigned to a product. No crystal structure could be obtained yet, but we presume that the tris(cyclopentadienyl)lanthanide complexes **1a–1e** react with LiAlH₄ forming a hydrido complex either by abstraction of a Cp ligand and hydride exchange or by coordination of the hydroaluminate like it is described for several cyclopentadienyl transition and rare earth metal complexes in literature.^[25] This active hydrido species reacts with the fluoroorganic compound yielding the HDF products and a fluoride lanthanide complex, which reacts with the hydride source reforming the active hydrido species.

The precatalysts show different reactivity trends depending on the applied substrate. One reason for this must lie in the gradual contraction of the ionic radii of the rare earth metals, which leads to different steric effects between the active species and the substrate depending on the applied lanthanide complex. The approach of the substrate may be hindered. Electronic effects should play a role as well and contribute to the stabilization or destabilization of transition states.

We could demonstrate that **1a–1e** can catalyze the hydrodefluorination of various fluorinated substrates (olefinic and aro-

matic), introducing the first reported rare earth metal catalyzed C–F bond activation. LiAlH₄ was used as hydride source. The precatalyst with the highest conversion for hexafluoropropene (6) is precatalyst **1e**, for the other substrates the precatalysts with larger ionic radii show higher reactivity. For **6** complete conversion to the hydrodefluorinated products and TONs up to 155 could be observed. HDF reactions of chlorotrifluoroethene (**13**) demonstrate that the C–F bond activation is favored over the C–Cl bond activation with a relatively high chemoselectivity, although regioselectvity and conversions were low.

Applying catalysts with different substitution patterns on the Cp ligand and variation of the central metal atom influences their steric and electronic properties and can lead to a lower or even higher reactivity and selectivity. Further studies to optimize the rare earth metal-catalyzed C–F bond activation and to clarify the mechanism are currently in progress.

Experimental Section

All preparations and reactions were performed using standard Schlenktype and vacuum line techniques, or by working in an argon-filled glove box. The amount of gaseous compounds was determined by using pVT techniques or by condensing the gas into a weighted J. Young flask. Toluene was distilled from potassium. **1a–1e** (abcr, Strem), **4a** (Sigma Aldrich), **7f** (Syn-Quest Labs), **11** (SCM Specialty Chemicals), and **13** (J. T. Baker Chemical Co.) were obtained from commercial sources and used as received. **15** was purchased from abcr and distilled from calcium hydride. **4b** was obtained from Sigma Aldrich, recrystallized from diethyl ether, and thoroughly dried under high vacuum for one day and night. **6** (Solvay) was obtained free of charge. All NMR spectra were recorded at 293 K with a JEOL JNM-ECS400 (¹H, ¹⁹F NMR; 399.65, 376.0 MHz).

Catalytic Hydrodefluorination: Reaction conditions and substrates are listed in Tables S1-S6 (Supporting Information). A single-necked flask equipped with a J. Young valve was charged with one of the precatalysts, the hydride source 4a-4b or 5 and solvent (2 mL). The solubility of **1a-1e** and **4b** is poor in toluene. The substrate (1 mmol, 1 equiv.) was added with a syringe and the mixture was degassed. Gaseous substrates (1 mmol, 1 equiv.) were condensed into the flask to the prior degassed mixture. The corresponding reaction conditions were applied. The crude reaction mixture was purified by fractional condensation under vacuum to a trap kept at -80 °C (for liquid substrates) or through two subsequent traps kept at -80 and -196 °C, respectively, for gaseous substrates. Fluorobenzene was added to the contents of the trap (liquid substrates) and a defined amount of that mixture was added to an NMR tube containing C₆D₆. The contents of the second trap (gaseous substrates) were condensed into a NMR tube containing a standard C₆D₆ solution of fluorobenzene.

The conversion of the substrates was determined by NMR spectra by integration of product resonances vs. the internal standard (fluorobenzene). The products were identified by ¹⁹F NMR spectroscopy ([D₆]benzene), using available literature data for 7a-7b,^[26] 7c,^[27] 7d-7e,^[28] 8a-8c,^[29] 8d,^[27] 9b,^[30] 10a-10c,^[31] 12a-12c,^[32] 14a-14d,^[33] 16a,^[34] 16b,^[35] or by comparison with an authentic sample (11, 9a, 12d).

CAUTION: Mixtures of fluorocarbons and alanes or $LiAlH_4$ are thermodynamically unstable and can lead to explosions. DIBAL is pyrophoric and the $LiAlH_4$ residue, if it still contains any ether, is also extremely pyrophoric.

Supporting Information (see footnote on the first page of this article): Experimental Section, Tables, Formulas, NMR spectrum of **1e**, BDEs.

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Keywords: Lanthanides; Catalysis; Hydrodefluorination; Lithium aluminum hydride

References

- a) M. Nishiura, F. Guo, Z. Hou, Acc. Chem. Res. 2015, 48, 2209–2220; b) J. Gromada, J.-F. Carpentier, A. Mortreux, Coord. Chem. Rev. 2004, 248, 397–410; c) Z. Hou, Y. Wakatsuki, Coord. Chem. Rev. 2002, 231, 1–22; d) R. Taube, H. Windisch, H. Weiβenborn, H. Hemling, H. Schumann, J. Organomet. Chem. 1997, 548, 229–236; e) K. C. Hultzsch, T. P. Spaniol, J. Okuda, Organometallics 1997, 16, 4845–4856; f) W. E. Piers, J. E. Bercaw, J. Am. Chem. Soc. 1990, 112, 9406–9407.
- [2] a) G. A. Molander, J. A. C. Romero, *Chem. Rev.* 2002, *102*, 2161–2186; b) C. M. Haar, C. L. Stern, T. J. Marks, *Organometallics* 1996, *15*, 1765–1784; c) V. P. Conticello, L. Brard, M. A. Giardello, Y. Tsuji, M. Sabat, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* 1992, *114*, 2761–2762; d) G. Jeske, H. Lauke, H. Mauermann, H. Schumann, T. J. Marks, *J. Am. Chem. Soc.* 1985, *107*, 8111–8118; e) W. J. Evans, J. H. Meadows, W. E. Hunter, J. L. Atwood, *J. Am. Chem. Soc.* 1984, *106*, 1291–1300.
- [3] a) M. Konkol, M. Kondracka, P. Voth, T. P. Spaniol, J. Okuda, *Organometallics* 2008, 27, 3774–3784; b) H. Schumann, M. R. Keitsch, J. Demtschuk, G. A. Molander, J. Organomet. Chem. 1999, 582, 70–82; c) H. Schumann, M. R. Keitsch, J. Winterfeld, S. Mühle, G. A. Molander, J. Organomet. Chem. 1998, 559, 181– 190; d) P.-F. Fu, L. Brard, Y. Li, T. J. Marks, J. Am. Chem. Soc. 1995, 117, 7157–7168; e) G. A. Molander, M. Julius, J. Org. Chem. 1992, 57, 6347–6351.
- [4] a) T. E. Müller, K. C. Hultzsch, M. Yus, F. Foubelo, M. Tada, *Chem. Rev.* 2008, 108, 3795–3892; b) S. Hong, T. J. Marks, Acc. *Chem. Res.* 2004, 37, 673–686; c) Y. Li, T. J. Marks, Organometallics 1996, 15, 3770–3772.
- [5] a) I. Beletskaya, A. Pelter, *Tetrahedron* 1997, 53, 4957–5026; b)
 P. Ji, T. Sawano, Z. Lin, A. Urban, D. Boures, W. Lin, *J. Am. Chem. Soc.* 2016, 138, 14860–14863.
- [6] Y.-R. Luo, in Comprehensive Handbook of Chemical Bond Energies, CRC Press, Boca Raton, 2007.
- [7] a) J.-P. Bégué, D. Bonnet-Delpon, in *Bioorganic and Medicinal Chemistry of Fluorine*, John Wiley & Sons, Inc., 2007, pp. 353–365; b) P. Kirsch, in *Modern Fluoroorganic Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2005; c) K. Uneyama, *Fundamentals in Organic Fluorine Chemistry*, Blackwell Publishing 2007; d) D. O'Hagan, *J. Fluorine Chem.* 2010, *131*, 1071–1081; e) D. O'Hagan, *Chem. Soc. Rev.* 2008, *37*, 308–319; f) B. E. Smart, *J. Fluorine Chem.* 2001, *109*, 3–11.
- [8] K. P. Shine, W. T. Sturges, Science 2007, 315, 1804–1805.
- [9] a) Q. Shen, Y.-G. Huang, C. Liu, J.-C. Xiao, Q.-Y. Chen, Y. Guo, J. Fluorine Chem. 2015, 179, 14–22; b) M. F. Kuehnel, D. Lentz, T. Braun, Angew. Chem. Int. Ed. 2013, 52, 3328–3348; c) T. Ahrens, J. Kohlmann, M. Ahrens, T. Braun, Chem. Rev. 2015, 115, 931–972; d) J. L. Kiplinger, T. G. Richmond, C. E. Osterberg, Chem. Rev. 1994, 94, 373–431; e) H. Amii, K. Uneyama, Chem. Rev. 2009, 109, 2119–2183; f) S.-D. Yang, Z.-J. Shi, in Homogeneous Catalysis for Unreactive Bond Activation, John Wiley & Sons, Inc., 2014, pp. 203–268; g) O. Eisenstein, J. Milani, R. N. Perutz, Chem. Rev. 2017, 117, 8710–8753; h) M. K. Whittlesey, E. Peris, ACS Catal. 2014, 4, 3152–3159.

- [10] a) H. Yin, A. J. Lewis, P. Carroll, E. J. Schelter, *Inorg. Chem.* 2013, *52*, 8234–8243; b) S. Alvarez, B. Menjón, *Angew. Chem. Int. Ed.* 2014, *53*, 2810–2811; c) H. Yin, A. V. Zabula, E. J. Schelter, *Dalton Trans.* 2016, *45*, 6313–6323.
- [11] G. B. Deacon, C. M. Forsyth, J. Sun, *Tetrahedron Lett.* 1994, 35, 1095–1098.
- [12] a) M. Klahn, U. Rosenthal, Organometallics 2012, 31, 1235– 1244; b) T. Kumar, F. Massicot, D. Harakat, S. Chevreux, A. Martinez, K. Bordolinska, P. Preethalayam, R. Kokkuvayil Vasu, J.-B. Behr, J.-L. Vasse, F. Jaroschik, Chem. Eur. J. 2017, 23, 16460–16465.
- [13] G. B. Deacon, A. J. Koplick, W. D. Raverty, D. G. Vince, J. Organomet. Chem. 1979, 182, 121–141.
- [14] a) C. J. Burns, R. A. Anderson, J. Chem. Soc., Chem. Commun. 1989, 136–137; b) P. L. Watson, T. H. Tulip, I. Williams, Organometallics 1990, 9, 1999–2009.
- [15] J. H. Melman, T. J. Emge, J. G. Brennan, *Inorg. Chem.* 2001, 40, 1078–1081.
- [16] a) L. Maron, E. L. Werkema, L. Perrin, O. Eisenstein, R. A. Andersen, J. Am. Chem. Soc. 2005, 127, 279–292; b) E. L. Werkema, E. Messines, L. Perrin, L. Maron, O. Eisenstein, R. A. Andersen, J. Am. Chem. Soc. 2005, 127, 7781–7795; c) E. L. Werkema, R. A. Andersen, L. Maron, O. Eisenstein, Dalton Trans. 2010, 39, 6648–6660.
- [17] G. B. Deacon, P. C. Junk, D. Werner, Eur. J. Inorg. Chem. 2015, 2015, 1484–1489.
- [18] A. D. Jaeger, C. Ehm, D. Lentz, submitted to Chem. Eur. J. 2018.
- [19] C. Janiak, Z. Anorg. Allg. Chem. 2010, 636, 2387-2390.
- [20] a) M. Konkol, T. P. Spaniol, M. Kondracka, J. Okuda, *Dalton Trans.* 2007, 4095–4102; b) L. Luconi, D. M. Lyubov, C. Bianchini, A. Rossin, C. Faggi, G. K. Fukin, A. V. Cherkasov, A. S. Shavyrin, A. A. Trifonov, G. Giambastiani, *Eur. J. Inorg. Chem.* 2010, 2010, 608–620; c) G. G. Skvortsov, A. O. Tolpyguin, G. K. Fukin, A. V. Cherkasov, A. A. Trifonov, *Eur. J. Inorg. Chem.* 2010, 2010, 1655–1662.
- [21] a) C. Schädle, R. Anwander, *Eur. J. Inorg. Chem.* 2013, 2013, 3302–3306; b) C. Schädle, C. Maichle-Mössmer, K. W. Törnroos, R. Anwander, *Organometallics* 2015, 34, 2667–2675; c) C. Schädle, A. Fischbach, E. Herdtweck, K. W. Törnroos, R. Anwander, *Chem. Eur. J.* 2013, 19, 16334–16341.
- [22] a) P. Arndt, A. Spannenberg, W. Baumann, V. V. Burlakov, U. Rosenthal, S. Becke, T. Weiss, *Organometallics* 2004, 23, 4792–4795; b) U. Jäger-Fiedler, M. Klahn, P. Arndt, W. Baumann, A. Spannenberg, V. V. Burlakov, U. Rosenthal, *J. Mol. Catal. A* 2007, 261, 184–189.

- [23] a) W. F. Edgell, L. Parts, J. Am. Chem. Soc. 1955, 77, 5515–5517;
 b) D. J. B. F. J. Mettille, Fluorine Chem. Rev. 1967, 1, 315–358;
 c) H.-J. Frohn, V. V. Bardin, J. Fluorine Chem. 2003, 123, 43–49;
 d) J.-J. Wu, J.-H. Cheng, J. Zhang, L. Shen, X.-H. Qian, S. Cao, Tetrahedron 2011, 67, 285–288.
- [24] a) K. Fuchibe, K. Mitomi, R. Suzuki, T. Akiyama, *Chem. Asian J.* 2008, *3*, 261–271; b) J. Cheng, J. Wu, S. Cao, *Tetrahedron Lett.* 2011, *52*, 3481–3484; c) T. Akiyama, K. Atobe, M. Shibata, K. Mori, *J. Fluorine Chem.* 2013, *152*, 81–83.
- [25] a) B. M. Bulychev, S. E. Tokareva, G. L. Soloveichick, E. V. Evdokimova, J. Organomet. Chem. 1979, 179, 263–273; b) J. A. Labinger, K. S. Wong, J. Organomet. Chem. 1979, 170, 373–384; c) Y. K. Gun'ko, B. M. Bulychev, A. I. Sizov, V. K. Bel'sky, G. L. Soloveichik, J. Organomet. Chem. 1990, 390, 153–158; d) S. Y. Knjazhanskij, B. M. Bulychev, O. K. Kireeva, V. K. Belsky, G. L. Soloveichik, J. Organomet. Chem. 1991, 414, 11–22; e) S. Y. Knjazhanski, E. S. Kalyuzhnaya, L. E. Elizalde Herrera, B. M. Bulychev, A. V. Khvostov, A. I. Sizov, J. Organomet. Chem. 1997, 531, 19–25; f) M. E. Burin, A. A. Logunov, G. K. Fukin, M. N. Bochkarev, J. Coord. Chem. 2009, 62, 3134–3141; g) R. Charles, R. González-Hernández, E. Morales, J. Revilla, L. E. Elizalde, G. Cadenas, O. Pérez-Camacho, S. Collins, J. Mol. Catal. A 2009, 307, 98–104.
- [26] H. Koroniak, K. W. Palmer, W. R. Dolbier, H.-Q. Zhang, Magn. Reson. Chem. 1993, 31, 748–751.
- [27] M. F. Kühnel, D. Lentz, Angew. Chem. Int. Ed. 2010, 49, 2933– 2936.
- [28] A. Foris, Magn. Reson. Chem. 2004, 42, 534-555.
- [29] R. N. Haszeldine, D. W. Keen, A. E. Tipping, J. Chem. Soc. C 1970, 414–421.
- [30] Y. L. Yagupolskii, N. V. Pavlenko, S. V. Shelyazhenko, A. A. Filatov, M. M. Kremlev, A. I. Mushta, I. I. Gerus, S. Peng, V. A. Petrov, M. Nappa, *J. Fluorine Chem.* **2015**, *179*, 134–141.
- [31] V. W. Weiss, P. Beak, W. H. Flygare, J. Chem. Phys. 1967, 46, 981–988.
- [32] J. W. Emsley, L. Phillips, Prog. Nucl. Magn. Reson. Spectrosc. 1971, 7, 1–520.
- [33] H. J. Osten, C. J. Jameson, N. C. Craig, J. Chem. Phys. 1985, 83, 5434–5441.
- [34] B. M. Kraft, W. D. Jones, J. Organomet. Chem. 2002, 658, 132– 140.
- [35] J. Bailey, R. G. Plevey, J. C. Tatlow, J. Fluorine Chem. **1987**, 37, 1–14.

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SHORT COMMUNICATION

<i>A. D. Jaeger, D. Lentz</i> [*] 1–6 Rare Earth Metal Catalyzed C–F Bond Activation	$C_{x}F_{n} \xrightarrow{5 \% Cp_{3}Ln} C_{x}F_{n-1}H$	
Kare Larin Wetar Cataryzed C-r Dond Activation	toluene, 80 °C	