CHEMISTRY
AN ASIAN JOURNAL
www.chemasianj.org

Accepted Article

Title: Gallium Hydrides and O/N-donors as tunable systems in C-F Bond Activation

Authors: Alma Dorothea Jaeger, Ruben Walter, Christian Ehm, and Dieter Lentz

To be cited as: *Chem. Asian J.* 10.1002/asia.201801030

Link to VoR: http://dx.doi.org/10.1002/asia.201801030

A Journal of
ACES
Asian Chemical Editorial Society

A sister journal of Angewandte Chemie and Chemistry – A European Journal

WILEY-VCH

Chemistry - An Asian Journal 10.1002/asia.201801030

WILEY-VCH

FULL PAPER

Gallium Hydrides and O/N-Donors as Tunable Systems in C-F Bond Activation

Alma D. Jaeger,[a] Ruben Walter,[a] Christian Ehm,*[b] and Dieter Lentz*[a]

Dedicated to Prof. Dietmar Stalke on the occasion of his 60th birthday

Abstract: The gallium hydrides $(iBu)_2GaH$ (**1a**), $LiGaH_4$ (**1b**) and $Me_3N{\cdot}GaH_3$ (**1c**) hydrodefluorinate vinylic and aromatic C-F bonds when O and N donor molecules are present. **1b** exhibits the highest reactivity. Quantitative conversion to the hydrodefluorination (HDF) products could be observed for hexafluoropropene and 1,1,3,3,3,-pentafluoropropene, 94 % conversion of pentafluoropyridine and 49 % of octafluorotoluene. Whereas for the HDF with **1b** high conversions are observed when catalytic amounts of O donor molecules are added, for **1a** the addition of N donor molecules lead to higher conversions. The *E*/*Z* selectivity of the HDF of 1,1,3,3,3-pentafluoropropene is donor dependent. DFT studies show that HDF proceeds in this case via the gallium hydride dimer-donor species and a hydrometallation/elimination sequence. Selectivities are sensitive to the choice of donor, as the right donor can lead to an on/off switching during catalysis, i.e. the hydrometallation step is accelerated by the presence of a donor, but the donor dissociates prior to elimination, allowing the inherently more selective donor-less gallium systems to determine the selectivity.

Introduction

Gallium hydrides are applied in metal-organic chemical vapour depositon (MOCVD) technology[1], hydrogallation[2] and more recently as active Lewis pairs in C-H bond activation.[3] Nonetheless, the chemistry of gallanes is scarcely scrutinized and far less investigated compared to alanes and boranes. Stabilization of gallane and alane (MH_3) can be achieved by the formation of adducts with Lewis bases like phosphanes or amines.[1c,4] In general, aluminum has a stronger tendency to form hyper-valent structures than gallium.[1c,4a] The less polarized Ga-H bond results in a weaker Lewis acidity of gallanes, which usually results in a lower reactivity compared to alanes.[1c,2b,4a,5] However, earlier studies showed that gallane complexes are milder and more selective reducing agents than similar alane complexes and exhibit a higher selectivity in hydrogallation reactions than the corresponding alanes in hydroalumination reactions.[2a,2b,4b,6] For example, the hydroalumination of 1,4-bis(trimethylsilylethynyl)benzene with di(*tert*-butyl)aluminum hydride yields the *cis*-product, which slowly isomerizes at elevated temperatures to the thermodynamically favored *trans*-product.[7] However, the reaction with di(*tert*-butyl)gallium hydride gave almost quantitatively the *cis*-product and rearrangement to the *trans*-form was not observed even after continued heating.[8]

In continuation of our studies concerning the organocatalytic hydrodefluorination (HDF) of several olefinic and aromatic fluorinated compounds with aluminum hydrides[9], we were interested in exploring the reactivity of gallium hydrides for C-F bond activation.

The C-F bond is one of the strongest single bonds with a bond dissociation energy (BDE) of approximately 120 kcal/mol.[10] The introduction of fluorine into organic molecules increases their thermodynamic and kinetic stability as well as their lipophilicity. This aspect is utilized in a wide range of applications, for example in pharmaceuticals, agrochemicals, highly stable polymers like Teflon, imaging agents or optoelectronics.[11] However, the inertness of the C-F bond has also led to environmental concerns.[12] Therefore, the activation of the C-F bond is of high interest in matters of degradation of highly fluorinated compounds, but as well for the synthesis of pharmaceutic building blocks from perfluorinated small molecules. Several systems, often transition metal based, are known for the catalytic HDF of olefinic and aromatic fluorinated compounds.[13] However, in many instances, transition-metal-catalyzed HDF reactions show low turn-over numbers (TON), caused by the strong affinity between transition metals and fluorine atoms, which leads to catalyst deactivation. A new approach is the use of silicon-, boron- and aluminum-based Lewis acids for the heterolytic fluoride abstraction from aliphatic fluorides.[14] Recently, Zhang reported an example for transition-metal-free, photocatalytic HDF of several polyfluoroarenes by pyrene-based photocatalysts[15]; and Ogoshi showed that the HDF of polyfluoroarenes can be catalyzed by hydrosilicates.[16]

Here, we present the C-F bond activation of per- and polyfluorinated substrates with gallium hydrides and O or N donor molecules.

Results and Discussion

Hexafluoropropene (**3**) is hydrodefluorinated by diisobutylgallium hydride (**1a**), lithium gallium hydride (**1b**) and the trimethylamine-galliumhydride adduct (**1c**) in donor solvents at ambient temperatures (Table 1). The HDF reactions lead to the formation of the *E*- and *Z*-isomer of 1,2,3,3,3-pentafluoropropene (**4a,b**);

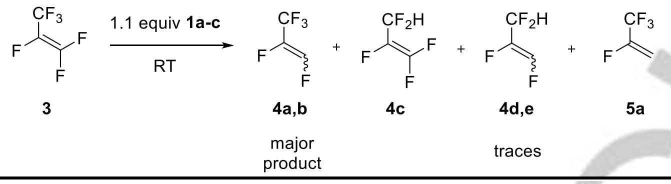
---

[a] A. D. Jaeger, R. Walter, Prof. Dr. D. Lentz
Freie Universität Berlin
Institut für Chemie und Biochemie, Anorganische Chemie,
Fabeckstr. 34-36, 14195 Berlin (Germany)
E-mail: dieter.lentz@fu-berlin.de
[b] Dr. C. Ehm
Università di Napoli Federico II
Dipartimento di Scienze Chimiche
Via Cintia, 80126 Napoli (Italy)

Supporting information for this article is given via a link at the end of the document.

10.1002/asia.201801030

Table 1. HDF of hexafluoropropene (**3**) with 1.1 equivalents of the gallium hydrides **1a-c** at RT.



Entry	Gallium hydride	Time [h]	Solvent	Donor additive	Donor [mol%]	*E*/*Z*	Conv. [%]	TON
1	**1a**	19	toluene	-	-	-	-	-
2	**1a**	21	diglyme	-	-	2.0	76.5	-
3	**1a**	16	NEt_3	-	-	1.9	95.5	-
4	**1a**	16	toluene	diglyme	12	1.8	5.1	0.4
5	**1a**	21	toluene	NEt_3	11	1.8	54.7	5.0
6	**1a**	21	toluene	NEt_3	33	1.9	81.1	2.5
7	**1b**	18	toluene	-	-	1.6	0.8	-
8	**1b**	0.25	diglyme	-	-	3.2	99.7	-
9	**1b**	18	diglyme	-	-	2.8	100	-
10	**1b**	15	NEt_3	-	-	1.5	97.0	-
11	**1b**	22	toluene	diglyme	10	1.6	96.4	10.7
12	**1b**	18	toluene	NEt_3	11	1.6	86.6	8.9
13	**1c**	16	toluene	-	-	2.9	14.2	-
14	**1c**	21	diglyme	-	-	2.9	80.7	-
15	**1c**	22	toluene	diglyme	15	1.7	29.7	2.0

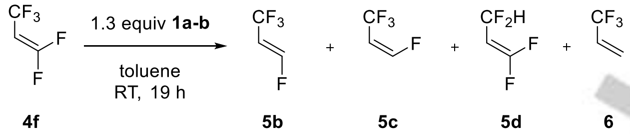
[a] Reaction conditions: 1 mmol **3**, 1.1 equiv. **1a-c** in toluene, diglyme or NEt_3 at RT. For full tables see the Supporting Information.

formation of the other constitutional isomer 1,1,2,3,3-pentafluoropropene, the 2nd generation HDF-products *E*- and *Z*-1,2,3,3-tetrafluoropropene (**4d,e**) and 2,3,3,3-tetrafluoropropene (**5a**) were observed in traces (see Supporting Information for full tables). Whereas for the HDF of **3** with **1b** nearly quantitative conversion to the HDF products could be observed after just 15 min reaction time in diglyme (entry 8), the reaction with **1a** yields 77 % conversion (entry 2) and the reaction with **1c** 81 % conversion to the HDF products after 21 h reaction time (entry 14). However, when the reaction is conducted in triethylamine the conversion increased to 96 % using **1a** (entry 3). In non-coordinating solvents the reactivity of the gallium hydrides is low; no HDF products are observed for the reaction of **3** with **1a** (entry 1), just traces for the reaction with **1b** (entry 7) and 14 % conversion with **1c** (entry 13) as this hydride already is a Lewis acid-base adduct. When catalytic amounts of diglyme (10 mol%) are added to **1b** in toluene, the conversion increases to 96 % (entry 11), i.e. the reaction is organocatalyzed by diglyme. However, the reaction of **3** and **1a** in toluene with addition of 12 mol% diglyme yields just 5 % conversion to the HDF products (entry 4). But when diglyme is replaced by 11 mol% trimethylamine 55 % conversion is observed (entry 5). The conversion can be further increased at higher temperatures (74 % conversion at 80 °C, see SI) or when the amount of triethylamine is increased (81 % conversion with 33 mol% NEt_3 at RT, entry 6). The HDF with **1c** is weakly catalyzed by donor solvents, as just a minor increase of the conversion is observed (entry 15).

In conclusion, **1a** shows a higher reactivity with N donors compared to O donors for the HDF of **3**, whereas just a small difference could be observed between the HDF reactions of **3** with **1b** in N or O donors. Slightly higher conversions are obtained with O donors and **1b**. The choice of solvent influences the *E*/*Z* selectivity just for the ionic compound $LiGaH_4$ (**1b**), which increases from 1.6 to 3.2 when the reaction is conducted in diglyme for 15 min.

Against our expectations the Lewis acid-base adduct **1c** does not show the expected HDF capability, although the conversion is slightly increased by addition of 15 mol% diglyme. That might be

Table 2. Catalytic HDF of 1,1,3,3,3-pentafluoropropene (**4f**) with 1.1 equivalents gallium hydrides **1a-b** at RT, overnight.



Entry	Gallium hydride	Solvent	Donor additive	Donor [mol%]	Main Products [%]		*E*/*Z*	Conv. [%]	TON
					5b	**5c**			
1	**1a**	toluene	-	-	-	-	-	-	-
2	**1a**	diglyme	-	-	47.3	4.0	11.8	53.1	-
3	**1a**	NEt_3	-	-	53.3	1.9	27.3	56.2	-
4	**1a**	toluene	THF	46	5.2	0.7	7.8	5.8	0.1
5	**1a**	toluene	NEt_3	36	33.1	1.6	20.6	35.2	1.0
6	**1a**	toluene	NEt_3	123	84.0	4.7	17.8	90.1	0.7
7	**1b**	toluene	-	-	1.7	0.9[b]	10.1	2.8	-
8	**1b**	toluene	diglyme	12	91.0	5.9	15.5	99.8	8.2

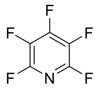
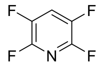
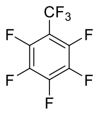
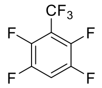
[a] Conversion is the sum of all HDF products (major and minor) and therefore may differ from the sum of the main products. For full tables see the Supporting Information. [b] Conversion of **5d**.

due to the fact that $Me_3N{\cdot}GaH_3$ (**1c**) is described as a mild reducing agent, which e.g. selectively reduces the carbonyl group in 4-bromophenylacyl bromide, but not the C-Br bond.[6] Therefore, **1c** was not applied in further HDF studies. The best results for the catalytic HDF of **3** with **1a** could be obtained with 30 mol% triethylamine and for **1b** with 10 mol% diglyme added to the toluene mixture. These conditions were applied for the subsequent HDF reactions.

Partially fluorinated propenes, as for example 1,1,3,3,3-pentafluoropropene (**4f**), show lower reactivity for HDF, but the selectivity is high. A remarkable *E*/*Z* ratio of 27 was observed for the HDF reaction with **1a**, *viz.* the thermodynamically more stable *E*-isomer of 1,3,3,3-tetrafluoropropene (**5b**) is preferentially formed. Such a high *E*/*Z* ratio is not observed in titanium-, rare-earth-metal-catalyzed or alane-induced HDF reactions; a maximum *E*/*Z* ratio of 15 was reported.[9,17] The conversion of the HDF reactions with **1a** in diglyme and NEt_3 are similar (53-56 %, entry 2,3), but the selectivity is much higher when the reaction is conducted in NEt_3. Selectivity is lower, when catalytic amounts of THF are used (entry 4). Interestingly, when 36 mol% NEt_3 are added to the toluene mixture of **1a** 35 % conversion (entry 5) could be observed, but when the amount of NEt_3 is increased to 123 mol%, 90 % conversion (entry 6) could be observed, which is higher compared to the reaction in pure NEt_3. The reaction with **1b** shows almost quantitative conversion with 12 mol% diglyme (entry 8).

To study the scope and limitations for the gallium hydride induced HDF, **1a** and **1b** were reacted with polyfluorinated aromatic

Table 3. Catalytic HDF of **7** and **9** with 1.1 equivalents of gallium hydrides **1a-b** in toluene at RT, overnight.

Entry	Substrate	HS[a]	Donor[b] [mol%]	Main Product [%]	Conv. [%]	TON
						
	7			**8a**		
1		**1a**	-	-	-	-
2		**1a**	34	52.1	52.1	1.5
3		**1b**	-	7.2	8.2	-
4		**1b**	10	90.3	93.5	10.1
						
	9			**10a**		
5		**1a**	-	-	-	-
6		**1a**	34	5.6	6.2	0.2
7		**1b**	-	1.1	1.2	-
8		**1b**	11	47.7	49.2	4.5

[a] HS = hydride sources. [b] Donor additives are NEt_3 for **1a** and diglyme for **1b**. [c] The amount of the conversion is the sum of all HDF products (major and minor) and therefore may differ from the sum of the main products. For full tables see the Supporting Information.

10.1002/asia.201801030

substrates (Table 3). The HDF of pentafluoropyridine (**7**) yields the expected *para*-substituted HDF product 2,3,5,6-tetrafluoropyridine (**8a**) as main product. In toluene without donor additive **1a** shows no reactivity, but **1b** (8 % conversion, entry 3) does. When 34 mol% NEt_3 are added, 52 % conversion could be observed for **1a** (entry 2). The reaction with **1b** can be catalyzed by adding 10 mol% diglyme resulting in 94 % conversion (entry 4). Octafluorotoluene (**9**) is predominantly hydrodefluorinated in *para*-position, forming heptafluorotoluene (**10a**). The reactivity is lower than for the other substrates. Just 6 % conversion could be observed when **1a** with 34 mol% NEt_3 were applied (entry 6). Similar to the reaction of **7**, the substitution reaction of **9** with **1b** could be catalyzed by 11 mol% diglyme with nearly 50 % conversion (entry 8). In contrast to 1.2 % without adding diglyme (entry 7).

Recent studies towards aluminum hydrides in C-F bond activation reactions showed that their reaction behavior coincide with the gallium hydrides. No or almost no HDF products could be observed for the HDF reactions with $(iBu)_2AlH$ (**2a**)[9] or $LiAlH_4$ (**2b**) in toluene, but with addition of catalytic amounts of donor molecules resulting in high conversions (Table 4). Comparison of the gallium hydrides **1a** and **1b** with corresponding aluminum hydrides **2a** and **2b** demonstrate that the reaction behavior of the ionic compounds **1b** and **2b** are similar: in the non-coordinating solvent toluene the conversion is low, but addition of 10 mol% diglyme increases the conversion up to 100 % for **3**, **4f** and **7** (compare Table 1-3 with 4). In contrast, **1a** is less reactive than **2a**. Whereas the HDF reactions with **2a** can be catalyzed by addition of 10 mol% diglyme, the HDF reactions with **1a** give higher conversions by addition of NEt_3 instead of diglyme. But even with ~ 30 mol% NEt_3 added to the HDF reactions using **1a**, the conversions are still lower than with **2a** (compare Table 1-3 with 4).

Table 4. HDF with 1.1 equivalents of aluminum hydrides **2a-b** in toluene at RT. Values for **2a** were taken from reference [9].

Entry	Substrate	HS[a]	Diglyme [mol%]	Conv. [%]	TON
1	**3**	**2a**	10.8	99.8	9.5
2	**3**	**2b**	10.5	100	11.0
3	**4f**	**2a**	12.4	59.3	4.8
4	**4f**	**2b**	12.5	100	8.3
5	**7**	**2a**	11.7	90.5	7.7
6	**7**	**2b**	10.1	100	10.2
7	**9**	**2a**	10.9	6.1	0.6
8	**9**	**2b**	10.4	42.7	4.1

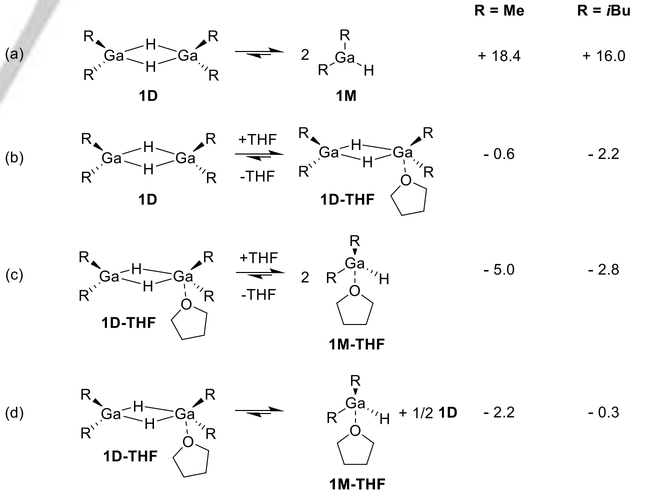
[a] HS = hydride sources. For full tables see the Supporting Information.

The ^{19}F-NMR spectra of the residue of the reaction of **3** with **1a** displayed a broad signal at -160.7 ppm, which we assigned to a gallium fluoride species as known shifts for Al-F compounds lie in the same range.[18] Thus, this can be seen as evidence for the hydrogen-fluorine-exchange from the gallane to the fluorinated substrate. However, no well-defined gallium compounds could be detected.

Mechanistic DFT Studies

Monomer-dimer-donor equilibria. We have recently shown that HDF using aluminum hydrides and O or N donors proceeds via the aluminum dimer donor adduct.[9] The donor is located far away from the active center in the TS and the exact nature of the donor thus does not influence the selectivity of the HDF reaction. The dimerization energies for Group 13 hydrides[19] as well as metal-hydride bond energies[10] decrease for the heavier group homologues and we postulated that they therefore hold the potential of offering higher selectivity.

To model the HDF reaction by computational chemistry, we chose **4f** and the gallium hydride $HGaMe_2$ (**1M**) and the donor THF. The Gibbs free energy of two molecules **1M** forming the gallium hydride dimer **1D** is predicted to be 18.4 kcal/mol or ~7 kcal/mol lower than for the corresponding aluminum compound (Scheme 1). Additionally, THF binds only very weakly to the dimer **1D** (-0.6 kcal/mol), forming **1D-THF**. Due to the weak dimerization energies of gallium hydrides, **1D-THF** is unstable with respect to the decomposition into **1M-THF** and **1D** (-2.2 kcal/mol), making **1M-THF** the most stable gallium hydride donor species, even if only sub-stoichiometric amounts of donor are added. This represents a marked difference to the aluminum system, where **1D-THF** was found to be most stable under similar conditions. Bulkier R groups like *i*Bu on Ga lead only to minute changes, but the preference for **1M-THF** over **1D-THF** diminishes (-0.3 kcal/mol).



Scheme 1. Gibbs free energies for the $HGaMe_2$ monomer-dimer-donor equilibria. T = 273 K.

Due to the low dimerization and donor coordination energies in this system, we considered HDF to take place via all possible gallium hydride species, i.e. **1M**, **1M-THF**, **1D** and **1D-THF**.

10.1002/asia.201801030

Donor influence on the competition of σ-bond metathesis, hydrometallation, S_NV. As HDF via **1D** is associated with the highest barriers (> 32 kcal/mol, see supporting information), we will not discuss this pathway here any further. The lowest competing HDF pathways are shown in Figure 1. All TS are formed directly from the reactants, as formation of adducts between reactants is endergonic, similar to the corresponding aluminum system.

In the absence of donor molecules, i.e. in HDF via **1M**, hydrometallation (HM) via **TS4f-11(1M)** is strongly preferred over six-membered σ-bond metathesis TS (SBM TS) **TS4f-5d(1M)** (Figure 1, blue traces). Formation of four-membered SBM TS is associated with even higher barriers (see supporting information). The lowest TS, HM, still possesses a rather sizable barrier (26.5 kcal/mol), indicating minimal reactivity at 273 K.

Coordination of a donor to **1M** blocks the coordination vacancy at Ga. The donor coordinates much weaker to Ga than to corresponding Al system (~12 kcal/mol vs. 18 kcal/mol). Donor coordination lowers the barrier for HM via **TS4f-11(1M-THF)** by ~ 5 kcal/mol to 21.1 kcal/mol (black traces). Similar to aluminum systems, donor coordination renders the formation of SBM TS impossible. Instead, a switch to S_NV character occurs. S_NV **TS4f-IP(1M-THF)** (18.7 kcal/mol) is much lower in energy than HM and HDF via **1M-THF** would proceed via formation of an ion pair (**IP**) from which elimination is likely unselective.

HDF via HM at **1D-THF** can proceed via two different pathways (**TS4f-11_A(1D-THF)** and **TS4f-11_B(1D-THF)** (red traces). The former involves only a single Ga (23.9 kcal/mol), but the latter proceeds cooperatively, involving both Ga centers, which lowers the barrier by 3 kcal/mol to 20.9 kcal/mol.

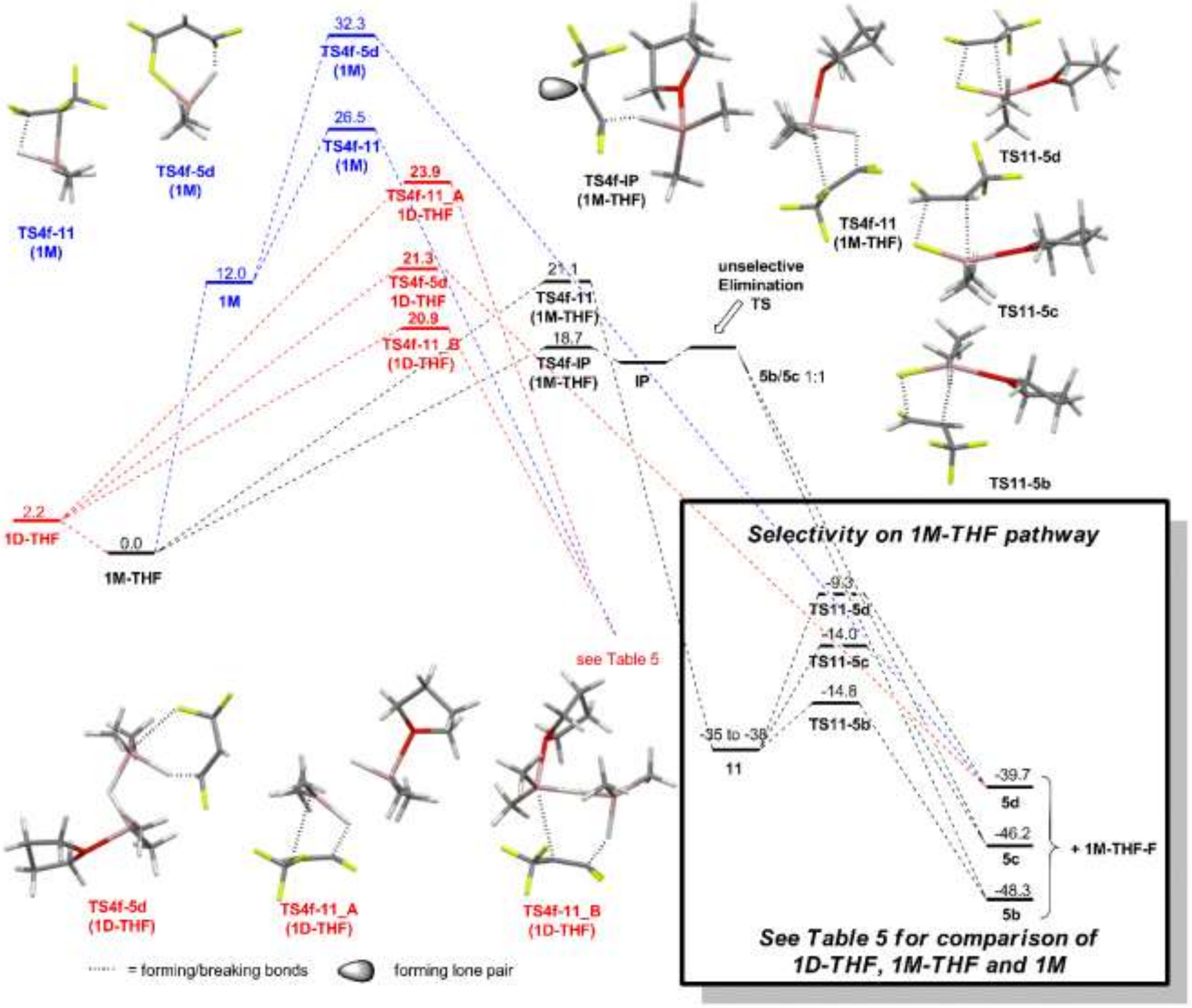


Figure 1. Lowest HDF reaction pathways for HDF of **4f** in the **1M** (blue traces), **1M-THF** (black traces) **and 1D-THF** (red traces) and corresponding transition state geometries. Hydrogen (white), carbon (grey), fluorine (yellow), aluminum (peach), oxygen (red). Structure labels for TS follow the notation TSreactant-product, e.g. **TS4f-5d** leads from **4f** to product **5d**. IP = ion pair. Gibbs free energies in kcal/mol, 273 K, solvent toluene.

10.1002/asia.201801030

Table 5. Relative Gibbs free energy differences of the transition states of the elimination step in the systems **1M**, **1M-THF**, **1D** and **1D-THF**. The free energy of **TS11-5b** has been set to 0. In kcal/mol, 273 K, solvent toluene.

	1M	1M-THF	1D	1D-THF
TS11-5b	0.0	0.0	0.0	0.0
TS11-5c	2.3	0.8	2.4	1.8
TS11-5d	6.8	5.5	6.4	6.3

HM barriers in the **1M-THF** and **1D-THF** system have comparable barriers (~21 kcal/mol) but unselective HDF via **TS4f-IP(1M-THF)** would be preferred in presence of a donor (18.7 kcal/mol). However, the four lowest barriers for HDF, either via **1M-THF** or **1D-THF** all lie within ~2.5 kcal/mol and bulky R groups on Ga can switch the preferred pathway, *vide infra*.

Donor influence on the selectivity in the hydrometallation/elimination pathway. HM leads in all systems to several energetically close lying resting states **11**. Elimination via **TS11-5(b-d)** is associated with considerable barriers (see Figure 1 and supporting information). Formation of **5b** via elimination is preferred by 0.8 kcal/mol over formation of **5c** in the **1M-THF** system and by 1.8 kcal/mol in the **1D-THF** system. Donor less systems **1M** and **1D** offer much higher selectivity at the elimination stage (~ 2.4 kcal/mol preference for formation of **5b**, Table 5). Elimination in the presence of THF proceeds via the **1D-THF** system (see Table 6).

In difference to aluminum systems, the donor is only weakly bound in the present gallium systems. Weaker Lewis bases (diglyme) or bulkier Lewis bases (NEt_3) than THF are therefore expected to bind even weaker in the TS, making elimination at the donor-less **1M** or **1D** preferred and thus increase selectivity. This is shown exemplary for **TS11-5b(1M-THF)** and **TS11-5b(1M-NEt_3)** in Figure 2.

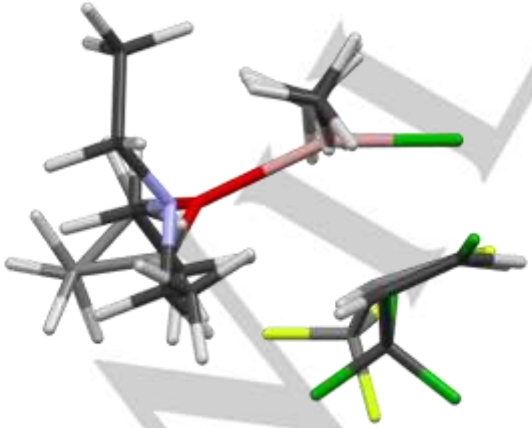


Figure 2. TS11-5b (1M-donor) for THF and NEt_3. Hydrogen (white), carbon (grey), fluorine (yellow), aluminum (peach), oxygen (red), nitrogen (indigo). Shown as an overlay, the more distorted $CFH=CHCF_3$ fragment (dark grey colored C atoms and green colored F atoms) belongs to **TS11-5b(1M-NEt_3)**. Ga-O distance 2.34 Å, Ga-N distance 2.71 Å.

The Ga-N distance must be increased much more than the Ga-O distance in the two TS. Additionally, the TS is much more distorted in the presence of the N-donor than in the presence of the O-donor THF. As shown in Table 6, this leads to a dramatic increase of the elimination TS energies in the **1M-NEt_3** system with respect to the lowest elimination pathway (**TS11-5b** +10.9 kcal/mol, only +1.8 kcal/mol in **1M-THF**). The donor effect is similar, albeit less dramatic for the **1D-NEt_3** system. This leads to a net preference for elimination from the donor-less **1D** system in the case of NEt_3. For THF, elimination via **1D-THF** is preferred over the donor-less pathways. The increased selectivity in the presence of NEt_3 was experimentally observed.

Table 6. Gibbs free energy differences of the transition states of the elimination step in the systems **1M**, **1M-donor**, **1D** and **1D-donor**. Donor = THF/NEt_3. The lowest absolute barrier has been set to 0; to bring all systems on the same scale CF_2CHCF_3 + **1D** + **1D-THF** was chosen as a reference point. In kcal/mol, 273 K, solvent toluene.

THF/NEt_3	1M	1M-donor	1D	1D-donor
TS11-5b	2.8/2.7	1.8/10.9	0.1/**0.0**	**0.0**/2.2
TS11-5c	5.2/5.0	2.6/11.6	2.6/**2.5**	**1.8**/4.6

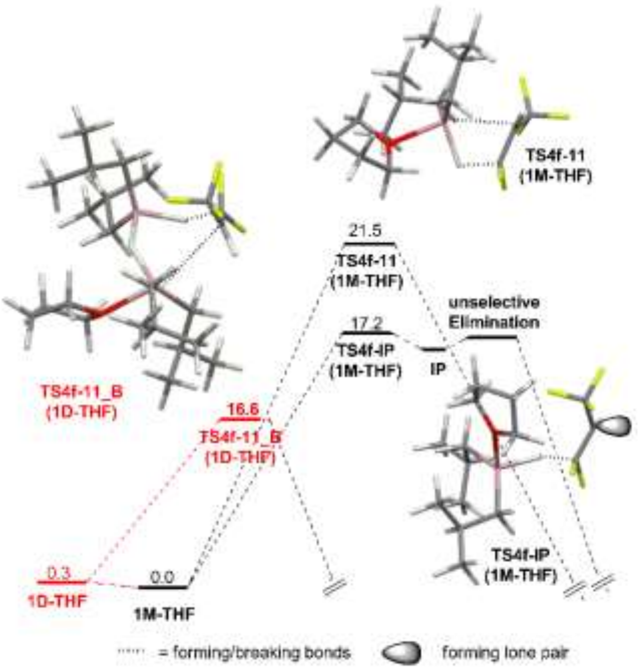


Figure 3. Lowest HDF reaction pathways for HDF of **4f** with HAl*i*Bu_2. Hydrogen (white), carbon (grey), fluorine (yellow), aluminum (peach), oxygen (red). Gibbs free energies in kcal/mol, 273 K, solvent toluene.

10.1002/asia.201801030

Influence of bulky R groups on gallium. The real system possesses bulkier *i*Bu groups, which shift the monomer-dimer equilibrium. This influences the balance between the HM and S_NV pathways. The preference for **1M-THF** over **1D-THF** is reduced by almost 2 kcal/mol (Scheme 1d), which favors all pathways proceeding via **1D-THF**. Re-optimization of the lowest lying **1M-THF** and **1D-THF** TS with *i*Bu groups shows that HM via **TS4f-11_B(1D-THF)** is slightly preferred (-0.6 kcal/mol) over unselective S_NV via **TS4f-IP(1M-THF)** (Figure 3). Unselective and selective HDF pathways lie energetically very close and the nature of the fluoro-olefin will influence selectivities. Only if a fluoro-olefin can stabilize a negative charge, unselective S_NV pathways are favored. This is experimentally observed for C_3F_6. Already C_3F_5H prefers an HM HDF pathway.

In summary, donor molecules lower the barrier for HDF at gallium hydride systems. Selectivities are substrate dependent but can be high for substrates with marginally stabilized anions, as HM becomes the dominant HDF pathway. In such a case, the selectivity can be tuned via the choice of donor. This is an indirect effect, as the presence of a donor during elimination decreases selectivity. The right choice of donor allows to accelerate the initial HM but forces the donor to dissociate before the selectivity determining elimination step.

Conclusions

Gallium hydrides activate vinylic and aromatic C-F bonds in the presence of catalytic amounts of O or N donor molecules. Conversions up to 100 % for the HDF of **3** and **4f** and high selectivity could be obtained for **4f**, **7** and **9**. $LiGaH_4$ (**1b**) exhibited the highest conversions followed by $(iBu)_2GaH$ (**1a**) and $Me_3N{\cdot}GaH_3$ (**1c**). The selectivity of the HDF of **4f** is donor dependent. DFT could demonstrate that the right choice of donor allows to accelerate the HDF reaction and to tune the selectivity. A high selectivity can be achieved by choosing weakly bound donors, which do not bound to the elimination TS, as the selectivity of the elimination step is higher in absence of a donor. The weak donor coordination energies of gallium hydrides are a pre-requisite for this on/off switch during organocatalysis.

Experimental Section

All preparations and reactions were performed using standard Schlenk-type 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. Diglyme, THF, *n*-pentane, diethyl ether and toluene were distilled from sodium or potassium. Trimethylamine hydrochloride, **2b** (Sigma Aldrich), **4f** (Syn-Quest Labs), $GaCl_3$ (abcr) were obtained from commercial sources and used as received. **7**, **9** were purchased from abcr and distilled from calcium hydride. **3** (Solvay) was obtained free of charge. **1b,c**[20] were synthesized as described in the corresponding literature. **1a** was synthesized from iBu_2GaCl analog the method of Petrov[21]. iBu_2GaCl (27.3 mmol) was dissolved in Et_2O, cooled to -80 °C and then LiH (114.6 mmol) was added in portions. After the mixture warmed to room temperature, it was stirred for 1 hour, filtered and the solvent was removed in vacuo. 67 % of **1a** was obtained as a colorless liquid and characterized according to the literature.[22] iBu_2GaCl was synthesized and characterized as described by Kovar[23], but instead of benzene the reaction was conducted in toluene.

Catalytic hydrodefluorination

Reaction conditions and substrates are listed in table 1-4 and in table S1-4 of the Supporting Information. A single-necked flask equipped with a J. Young valve was charged with **1a**, **1b**, **1c**, **2a** or **2b**, organocatalyst and solvent. The substrate was added with a syringe and the mixture was degassed. Gaseous substrates 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 °C 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 C_6D_6. The contents of the second trap (gaseous substrates) were condensed into a NMR tube containing a standard C_6D_6 solution of fluorobenzene. The conversion of the substrates was determined by NMR spectra by integration of product resonances versus the internal standard (fluorobenzene). The products were identified by ^{19}F NMR spectroscopy (benzene-d_6), using available literature data for **4a-b**[24], **4c**[17a], **4d-e**[25], **5a-c**[26], **5d**[17a], **8a**[27], **8b**[28], **8c**[29], **10a**[30], **10b**[31], **10c**[29], **10d**[32], **10e**[33] or by comparison with an authentic sample (**4f**, **8d**, **6**).

Calculations. Starting geometries were generated by taking the optimized structures of the corresponding aluminum systems and replacing Al with Ga. All structures were fully optimized at the M06-2X(PCM)[34] /cc-pVDZ level of theory using Gaussian09[35] coupled to an external optimizer (PQS, OPTIMZE routine)[36] within the BOPT software package.[37] An fine grid and standard SCF convergence quality settings (Scf=tight) for Gaussian single point calculations were used. The nature of each stationary point was checked with an analytical second-derivative calculation (no imaginary frequency for minima, exactly one imaginary frequency for transition states, corresponding to the reaction coordinate). Solvent influence (toluene, $\varepsilon=2.3741$) was modelled explicitly during the optimization and SP step, using the polarizable continuum model (PCM) implemented in the Gaussian 09 software suite. The M06-2X functional has been shown to yield accurate results for systems involving group 13 systems.[9,38]

Vibrational analysis data derived at this level of theory were used to calculate thermal corrections (enthalpy and entropy, 298 K, 1 bar) for all species considered. Final single-point energies (SP) were calculated at the M06-2X(PCM)[39] level of theory employing triple-ζ Dunning basis sets (cc-pVTZ) from the EMSL basis set exchange library,[40] to minimize BSSE contributions.[41]

Acknowledgements

The authors would like to thank Prof. P. H. M. Budzelaar (University of Naples, Federico II., Italy) for generous donation of CPU time. Support from the Deutsche Forschungsgemeinschaft (DFG) Le423/17-1 and the GRK 1582 (Fluorine as a Key Element) is gratefully acknowledged.

Keywords: homogeneous catalysis • DFT • gallium hydrides • hydrodefluorination • organocatalyst

[1] a) A. M. Arif, B. L. Benac, A. H. Cowley, R. Geerts, R. A. Jones, K. B. Kidd, J. M. Power, S. T. Schwab, *J. Chem. Soc., Chem. Commun.* **1986**, 1543-1545; b) A. H. Cowley, R. A. Jones, M. A. Mardones, J. Ruiz, J. L. Atwood, S. G. Bott, *Angew. Chem. Int. Ed.* **1990**, *29*, 1150-1151; c) C. L. Raston, *J. Organomet. Chem.* **1994**, *475*, 15-24; d) A. C. Jones, *Chem. Soc. Rev.* **1997**, *26*, 101-110.

[2] a) W. Uhl, *Coord. Chem. Rev.* **2008**, *252*, 1540-1563; b) W. Uhl, M. Claesener, S. Haddadpour, B. Jasper, I. Tiesmeyer, S. Zemke, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2889-2896; c) W. Uhl, A. Hepp, H. Westenberg, S. Zemke, E.-U. Würthwein, J. Hellmann, *Organometallics* **2010**, *29*, 1406-1412; d) W. Uhl, J. Bohnemann, D. Heller, A. Hepp, M. Layh, *Z. Anorg. Allg. Chem.* **2012**, *638*, 68-75; e) W. Uhl, B. Kappelt, F. Kappelt, J. Bohnemann, M. Layh*, Vol. 71*, Zeitschrift für Naturforschung B, **2016**, pp. 509-520.

[3] W. Uhl, M. Willeke, F. Hengesbach, A. Hepp, M. Layh, *Organometallics* **2016**, *35*, 3701-3712.

[4] a) C. Jones, G. A. Koutsantonis, C. L. Raston, *Polyhedron* **1993**, *12*, 1829-1848; b) M. G. Gardiner, C. L. Raston, *Coord. Chem. Rev.* **1997**, *166*, 1-34; c) S. Aldridge, A. J. Downs, *Chem. Rev.* **2001**, *101*, 3305-3366; d) A. J. Downs, *Coord. Chem. Rev.* **1999**, *189*, 59-100.

[5] a) W. Uhl, A. Hentschel, D. Kovert, J. Kösters, M. Layh, *Eur. J. Inorg. Chem.* **2015**, *2015*, 2486-2496; b) J. J. Eisch, *J. Am. Chem. Soc.* **1962**, *84*, 3830-3836.

[6] C. L. Raston, A. F. H. Siu, C. J. Tranter, D. J. Young, *Tetrahedron Lett.* **1994**, *35*, 5915-5918.

[7] W. Uhl, F. Breher, *J. Organomet. Chem.* **2000**, *608*, 54-59.

[8] W. Uhl, H. R. Bock, F. Breher, M. Claesener, S. Haddadpour, B. Jasper, A. Hepp, *Organometallics* **2007**, *26*, 2363-2369.

[9] A. D. Jaeger, C. Ehm, D. Lentz, *Chem. Eur. J.* **2018**, *24*, 6769-6777.

[10] Y.-R. Luo, in *Comprehensive Handbook of Chemical Bond Energies*, CRC Press, Boca Raton, **2007**.

[11] a) P. Kirsch, in *Modern Fluoroorganic Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, **2005**; b) J.-P. Bégué, D. Bonnet-Delpon, in *Bioorganic and Medicinal Chemistry of Fluorine*, John Wiley & Sons, Inc., **2007**, 353-365; c) B. E. Smart, *J. Fluorine Chem.* **2001**, *109*, 3-11; d) M. P. Krafft, J. G. Riess, *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 1185-1198; e) T. Hiyama, H. Yamamoto, in *Organofluorine Compounds: Chemistry and Applications*, Springer Berlin Heidelberg, Berlin, Heidelberg, **2000**, 137-182; f) K. Müller, C. Faeh, F. Diederich, *Science* **2007**, *317*, 1881-1886; g) S. Purser, P. R. Moore, S. Swallow, V. Gouverneur, *Chem. Soc. Rev.* **2008**, *37*, 320-330; h) D. O'Hagan, *J. Fluorine Chem.* **2010**, *131*, 1071-1081; i) B. Ameduri, B. Boutevin, in *Well-Architectured Fluoropolymers: Synthesis, Properties and Applications*, Elsevier Science, Amsterdam, **2004**; j) K. Uneyama, *Fundamentals in Organic Fluorine Chemistry*, Blackwell Publishing, **2007**.

[12] a) C. M. Roehl, D. Boglu, C. Brühl, G. K. Moortgat, *Geophysical Research Letters* **1995**, *22*, 815-818; b) D. G. Victor, G. J. MacDonald, *Climatic Change* **1999**, *42*, 633-662; c) A. McCulloch, *J. Fluorine Chem.* **2003**, *123*, 21-29; d) A. R. Ravishankara, S. Solomon, A. A. Turnipseed, R. F. Warren, *Science* **1993**, *259*, 194-199.

[13] a) J. L. Kiplinger, T. G. Richmond, *Chem. Commun.* **1996**, 1115-1116; b) J. L. Kiplinger, T. G. Richmond, *J. Am. Chem. Soc.* **1996**, *118*, 1805-1806; c) J. Vela, J. M. Smith, Y. Yu, N. A. Ketterer, C. J. Flaschenriem, R. J. Lachicotte, P. L. Holland, *J. Am. Chem. Soc.* **2005**, *127*, 7857-7870; d) U. Jäger-Fiedler, M. Klahn, P. Arndt, W. Baumann, A. Spannenberg, V. V. Burlakov, U. Rosenthal, *J. Mol. Catal. A: Chem.* **2007**, *261*, 184-189; e) S. P. Reade, M. F. Mahon, M. K. Whittlesey, *J. Am. Chem. Soc.* **2009**, *131*, 1847-1861; f) M. F. Kuehnel, D. Lentz, T. Braun, *Angew. Chem. Int. Ed.* **2013**, *52*, 3328-3348; g) M. K. Whittlesey, E. Peris, *ACS Catalysis* **2014**, *4*, 3152-3159; h) T. Ahrens, J. Kohlmann, M. Ahrens, T. Braun, *Chem. Rev.* **2015**, *115*, 931-972; i) T. Ahrens, M. Ahrens, T. Braun, B. Braun, R. Herrmann, *Dalton Trans.* **2016**, *45*, 4716-4728; j) D. A. Baird, S. Jamal, S. A. Johnson, *Organometallics* **2017**, *36*, 1436-1446; k) R. Kojima, K. Kubota, H. Ito, *Chem. Commun.* **2017**, *53*, 10688-10691; l) H. Sakaguchi, Y. Uetake, M. Ohashi, T. Niwa, S. Ogoshi, T. Hosoya, *J. Am. Chem. Soc.* **2017**, *139*, 12855-12862; m) C. Ehm, J. Krüger, D. Lentz, *Chem. Eur. J.* **2016**, *22*, 9305-9310; n) J. Kruger, C. Ehm, D. Lentz, *Dalton Trans.* **2016**, *45*, 16789-16798; o) J. Krüger, J. Leppkes, C. Ehm, D. Lentz, *Chem. Asian J.* **2016**, *11*, 3062-3071.

[14] a) T. Stahl, H. F. T. Klare, M. Oestreich, *ACS Catalysis* **2013**, *3*, 1578-1587; b) V. J. Scott, R. Çelenligil-Çetin, O. V. Ozerov, *J. Am. Chem. Soc.* **2005**, *127*, 2852-2853; c) M. Klahn, C. Fischer, A. Spannenberg, U. Rosenthal, I. Krossing, *Tetrahedron Lett.* **2007**, *48*, 8900-8903; d) W. Gu, M. R. Haneline, C. Douvris, O. V. Ozerov, *J. Am. Chem. Soc.* **2009**, *131*, 11203-11212; e) C. Douvris, C. M. Nagaraja, C.-H. Chen, B. M. Foxman, O. V. Ozerov, *J. Am. Chem. Soc.* **2010**, *132*, 4946-4953.

[15] J. Lu, N. S. Khetrapal, J. A. Johnson, X. C. Zeng, J. Zhang, *J. Am. Chem. Soc.* **2016**, *138*, 15805-15808.

[16] K. Kikushima, M. Grellier, M. Ohashi, S. Ogoshi, *Angew. Chem. Int. Ed.* **2017**, *56*, 16191-16196.

[17] a) M. F. Kühnel, D. Lentz, *Angew. Chem. Int. Ed.* **2010**, *49*, 2933-2936; b) A. D. Jaeger, D. Lentz, *Z. Anorg. Allg. Chem.* **2018**, *DOI: 10.1002/zaac.201800044*.

[18] S. B. S. Berger, H.-O. Kalinowski, *19F-NMR-Spektroskopie, Vol. 4*, Georg Thieme Verlag, Stuttgart, **1994**.

[19] C. Ehm, G. Antinucci, P. H. M. Budzelaar, V. Busico, *J. Organomet. Chem.* **2014**, *772-773*, 161-171.

[20] N. N. Greenwood, A. Storr, M. G. H. Wallbridge, *Inorg. Chem.* **1963**, *2*, 1036-1039.

[21] V. A. K. V. V. Markova, A. A. Petrov, *Zh. Obshch. Khim.* **1967**, *37*, 1744-1748.

[22] W. Uhl, L. Cuypers, G. Geiseler, K. Harms, W. Massa, *Z. Anorg. Allg. Chem.* **2002**, *628*, 1001-1006.

[23] R. A. Kovar, H. Derr, D. Brandau, J. O. Callaway, *Inorg. Chem.* **1975**, *14*, 2809-2814.

[24] H. Koroniak, K. W. Palmer, W. R. Dolbier, H.-Q. Zhang, *Magn. Reson. Chem.* **1993**, *31*, 748-751.

[25] A. Foris, *Magn. Reson. Chem.* **2004**, *42*, 534-555.

[26] R. N. Haszeldine, D. W. Keen, A. E. Tipping, *J. Chem. Soc. C* **1970**, 414-421.

[27] J. Lee, K. G. Orrell, *J. Chem. Soc.* **1965**, 582-594.

[28] P. L. Coe, A. G. Holton, J. C. Tatlow, *J. Fluorine Chem.* **1982**, *21*, 171-189.

[29] S. M. Senaweera, A. Singh, J. D. Weaver, *J. Am. Chem. Soc.* **2014**, *136*, 3002-3005.

[30] B. M. Kraft, W. D. Jones, *J. Organomet. Chem.* **2002**, *658*, 132-140.

[31] J. Bailey, R. G. Plevey, J. C. Tatlow, *J. Fluorine Chem.* **1987**, *37*, 1-14.

[32] L. Schwartsburd, M. F. Mahon, R. C. Poulten, M. R. Warren, M. K. Whittlesey, *Organometallics* **2014**, *33*, 6165-6170.

[33] P. Novák, A. Lishchynskyi, V. V. Grushin, *Angew. Chem. Int. Ed.* **2012**, *51*, 7767-7770.

[34] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215-241.

[35] G. W. T. M. J. Frisch, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[36] a) J. Baker, *J. Comput. Chem.* **1986**, *7*, 385-395; b) J. Baker, PQS, 2.4 Parallel Quantum Solutions: Fayetteville, AR, 2001.

[37] P. H. M. Budzelaar, *J. Comput. Chem.* **2007**, *28*, 2226-2236.

[38] a) C. Ehm, G. Antinucci, P. H. M. Budzelaar, V. Busico, *J. Organomet. Chem.* **2014**, *772-773*, 161-171; b) C. Ehm, R. Cipullo, P. H. M. Budzelaar, V. Busico, *Dalton Trans.* **2016**, *45*, 6847-6855; c) F. Zaccaria, A. Vittoria, A. Correa, C. Ehm, P. H. M. Budzelaar, V. Busico, R. Cipullo, *ChemCatChem* **2018**, *10*, 984-988.

[39] a) R. Raucoules, T. de Bruin, P. Raybaud, C. Adamo, *Organometallics* **2009**, *28*, 5358-5367; b) S. Tobisch, T. Ziegler, *J. Am. Chem. Soc.* **2004**, *126*, 9059-9071.

[40] a) D. Feller, *J. Comput. Chem.* **1996**, *17*, 1571-1586; b) K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li, T. L. Windus, *Journal of Chemical Information and Modeling* **2007**, *47*, 1045-1052.

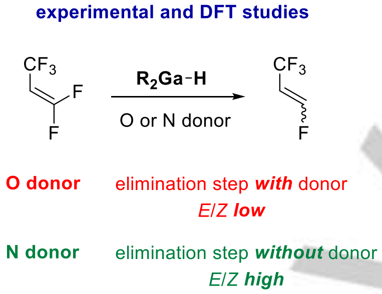
[41] S. F. Boys, F. Bernardi, *Mol. Phys.* **1970**, *19*, 553-566.

Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

O and N donor solvents activate gallium hydride bonds and enable the HDF of per- and polyfluorinated olefins and arenes under mild conditions. DFT studies elucidate the preferred mechanisms in respect to different alkyl groups at Ga and donors. The selectivity can be tuned via the choice of donor.



A. D. Jaeger, R. Walter, C. Ehm, D. Lentz**

Page No. – Page No.

Gallium Hydrides and O/N-donors as tunable systems in C-F Bond Activation

Layout 2:

FULL PAPER

((Insert TOC Graphic here; max. width: 11.5 cm; max. height: 2.5 cm))

*Author(s), Corresponding Author(s)**

Page No. – Page No.

Title

Text for Table of Contents

For internal use, please do not delete. Submitted_Manuscript