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Main group metal and transition metal complexes containing fluorinated β -diketiminato ligands

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

Abstract: The synthesis of fluorinated β -diketimine LH **1** (L = HC[C(CF₃)N(C₆F₅)₂]) and its reactions with main group and transition metal complexes, yielding LAIME₂ **4**, LZnEt **5**, LCu(C₆H₆) **6** and LCuCO **7**, is reported. **1** – **7** were characterized by IR and NMR spectroscopy (¹H, ¹³C, ¹⁹F), elemental analysis and single crystal X-ray diffraction. The C₆F₅ substituents strongly reduce the π -back-bonding capacity of the β -diketiminato ligand as was shown for **7** by IR spectroscopy.

Introduction

Monoanionic β -diketiminates HC[C(R)NR']₂ bearing sterically demanding aryl substituents (R') find widespread applications as N,N'-chelating ligands in metal organic chemistry.^[1] They show excellent properties in the stabilization of metal atoms in low coordination numbers and in low oxidation states, in particular of group 2,^[2] 12,^[3] 13,^[4] and 14.^[5] The ease with which their steric and electronic properties can be modified render them very promising for catalytic applications. For instance, zinc complexes HC[C(R)NR']₂ZnR" (R" = alkyl, amide NR₂, alkoxide OR) showed very high activity in the polymerization of cyclic esters such as lactide as well as in CO₂/epoxide co-polymerization.^[6] With respect to their role as kinetically-stabilizing substituent for low-valent metal complexes with low coordination number, sterically demanding β -diketiminates have been developed. Their steric demand is mainly controlled by the β -C and N-aryl *ortho*-substituents, whereas the electronic properties of β -diketiminates are mainly influenced by the γ -C and β -C positions.^[1b,7] The beneficial effect of electron-withdrawing groups in the backbone and at the nitrogen atom on the catalytic activity of β -diketiminato complexes as well as in the design of complexes with desirable ligand-based redox and optical properties has been demonstrated.^[8] Sadighi et al. introduced electron-poor β -diketiminato ligands bearing CF₃ groups in the backbone and in *meta*-position of the N-aryl groups,^[9] whereas the effect of adding electron-donating dialkylamino groups to the β -diketiminato backbone was recently reported.^[10] Transition metal β -diketiminato complexes bearing electron-withdrawing CF₃ groups in the backbone showed promising catalytic activities, which were

addressed to the higher Lewis acidity of the metal.^[11] In contrast, the influence of *meta*-CF₃ groups at the N-aryl substituent is less pronounced. The CO stretching vibration of L'CuCO complexes (L' = HC[C(CF₃)N(3,5-CF₃)₂C₆H₃])₂, which is directly related to the π -back-bonding strength of the Cu atom, is less influenced by *meta*-CF₃ groups compared to CF₃ groups at the backbone.^[9] Our interest in complexes containing N,N'- and N,O-chelating amidinate,^[12] β -diketiminates,^[13] β -ketoiminate,^[14] and ureate ligands^[15] prompted us to evaluate the influence of electron-withdrawing substituents in β -diketiminates on their electronic nature, leading to the synthesis of β -diketimine LH **1** (L = HC[C(CF₃)NC₆F₅])₂. **1** was further used as electron-withdrawing substituents in main group metal (LAIME₂ **4**) and transition metal complexes (LZnEt **5**, LCu(C₆H₆) **6** and LCuCO **7**).

Results and Discussion

1 was obtained as bright yellow solid (38 % yield) together with β -ketoenamine **2** (14 % yield) from the TiCl₄-catalyzed reaction of an excess of C₆F₅NH₂ with 1,1,1,5,5,5-hexafluoroacetylacetone (fac₂H) (Scheme 1).

Scheme 1. Synthesis of **1** and **2** using titanium tetrachloride.

Any attempt to lower the excess of C₆F₅NH₂ by adding NEt₃ gave **1** and **2** in lower relative yields. However, the second by-product **3** was formed and isolated by column chromatography and recrystallized from a solution in *n*-heptane (Scheme 2). **1** can not be thermally converted into **3** as was proven by heating a solution of **1** in toluene-d₈ to 105 °C for 12 h. The resulting ¹⁹F NMR spectrum only showed the resonances due to **1**, whereas no indication for the formation of **3** was found.

Scheme 2. Alternative synthesis of **1** and **2**, which is accompanied by formation of by-product **3** (ratio 1/2/3: y = 7, 0/0/28 %; y = 5.5, 22/10/10 %; y = 4, 25/16/3 %).

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In addition, the synthesis of **1** by an Aza-Wittig reaction failed.^[9] **2** was almost quantitatively formed by reaction of one equivalents of $\text{Ph}_3\text{P}=\text{NC}_6\text{F}_5$ with fac_2H at 105 °C for 12 h. Further reaction of **2** with a second equivalent of $\text{Ph}_3\text{P}=\text{NC}_6\text{F}_5$ was not observed even after heating for 7 days (Scheme 3).

Scheme 3. Aza-Wittig reaction as-described by *Sadighi et al.*^[9].

The ^1H NMR spectrum of **1** in CD_2Cl_2 shows a sharp singlet at 6.18 ppm for the $\gamma\text{-CH}$ group and a broad singlet at 10.99 ppm for the NH proton. The ^{19}F NMR spectrum shows three signals of the C_6F_5 groups at -147.9 ppm (dt, $^3J_{\text{FF}} = 20.9$ Hz, $^4J_{\text{FF}} = 4.1$ Hz) for the *ortho*-F, -156.9 ppm (t, $^3J_{\text{FF}} = 21.3$ Hz) for the *para*-F and -162.8 ppm (td, $^3J_{\text{FF}} = 21.5$ Hz, $^4J_{\text{FF}} = 5.3$ Hz) for the *meta*-F atoms. One triplet (t, $^6J_{\text{FF}} = 4.4$ Hz) for both CF_3 groups at -68.3 ppm proves C_{2v} -symmetry of **1** in solution. The triplet results from through-space F-F coupling of the CF_3 group (scheme 4, marked in red) with two *ortho*-F atoms of the C_6F_5 group, which was confirmed by ^{19}F - ^{19}F -COSY NMR spectroscopy (Fig. S5).^[16]

Scheme 4. Fluorine atoms in **1** - **3** responsible for through-space interactions (triplet resonance in the ^{19}F -NMR spectra) are highlighted in red; CF_3 -groups marked in blue are observed as singlets in the ^{19}F NMR spectra of **2** and **3**.

The ^{19}F NMR spectrum of **2** shows one triplet at -68.5 ppm (t, $^6J_{\text{FF}} = 5.0$ Hz) and one singlet of equal intensity at -78.5 ppm for the two CF_3 groups. The triplet is caused by through-space coupling of one CF_3 group with two *ortho*-F as was observed for **1**. The ^{19}F NMR spectrum of **3** also shows a triplet at -70.4 ppm (t, $^6J_{\text{FF}} = 7.6$ Hz) for the CF_3 -group next to C_6F_5 group, while the second CF_3 -group appears as singlet at -73.2 ppm.

The electronic properties and the reactivity of the NH and $\gamma\text{-CH}$ groups of **1** was evaluated in reactions with different metal complexes. **1** reacts with Me_3Al with CH_4 elimination and formation of **4** (scheme 5), which was obtained in 88% yield after recrystallization from a solution in *n*-hexane. Deprotonation of the $\gamma\text{-CH}$ group was never observed, even in the presence of a fourfold excess of Me_3Al and at elevated reaction temperatures (110 °C). Comparable results were found for the reaction of **1** with Et_2Zn in hexane (scheme 6), which proceeded with ethane elimination and formation of the heteroleptic complex LZnEt **5**. **5** was isolated in 85% yield after recrystallization from a solution in *n*-hexane. Deprotonation of the CH-group by reaction with an excess of Et_2Zn failed.

Scheme 5. Synthesis of **4** by reaction of **1** with an equimolar amount of Me_3Al .

Scheme 6. Synthesis of **5** by reaction of **1** with an equimolar amount of Et_2Zn .

We further investigated the role of the C_6F_5 group on the electronic properties of electron-rich copper complexes. The reaction of **1** with MesCu ($\text{Mes} = 2,4,6\text{-Me}_3\text{-C}_6\text{H}_2$) in C_6D_6 yielded $\text{LCu}(\text{C}_6\text{D}_6)$ **6**, which was isolated after workup as bright orange crystalline solid in 53% yield. In addition, the reaction of **6** with CO resulted in the formation of the carbonyl complex LCuCO **7**, which precipitated as a bright yellow solid upon thawing (scheme 7). **7** was isolated by centrifugation in 68% yield.

Scheme 7. Synthesis of compounds **6** and **7**.

^1H and ^{19}F NMR spectra of **6** and **7** show the expected resonances of the $\gamma\text{-CH}$ (5.87 **6**, 5.97 **7**) and the CF_3 groups (-66.1 (t, $^6J_{\text{FF}} = 4.1$ Hz) **6**; -65.6 (t, $^6J_{\text{FF}} = 5.2$ Hz) **7**) and the *ortho*-F (-148.8 (m) **6**; -148.6 (m) **7**), *para*-F (-159.2 (t, $^3J_{\text{FF}} = 22.6$ Hz, 2F) **6**; -157.8 (t, $^3J_{\text{FF}} = 22.1$ Hz) **7**) and *meta*-F (-163.4 (td, $^3J_{\text{FF}} = 23.6$ Hz, $^4J_{\text{FF}} = 6.2$ Hz, 4F) **6**; -162.5 (dt, $^3J_{\text{FF}} = 23.1$, $^4J_{\text{FF}} = 6.3$ Hz) **7**), proving the C_{2v} symmetric complexes as observed for **4** and **5**. **7** is stable in its crystalline form at -30 °C for several days, but decomposes at ambient temperature within a few hours. Solutions of **7** in benzene and toluene also decompose at ambient temperature even under CO-atmosphere with formation of Cu metal and a color change from yellow to brown. The resulting ^1H -NMR spectrum shows a shift of the backbone proton signal and the ^{19}F -NMR spectrum many additional resonances, which could not be addressed to any defined reaction product. In contrast, the decomposition of **7** in polar solvents such as dichloromethane occurs instantaneously. Due to the fast decomposition reactions, clean ^{13}C -NMR spectra of **7** could not be recorded. **7** loses CO rapidly under reduced pressure as was confirmed by IR spectroscopy.

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The IR spectrum of **7** shows absorption bands at 2135 cm⁻¹ and 2122 cm⁻¹, pointing to the presence of two different carbonyl complexes in the solid state. The signal intensities did not change over 24 h, eliminating the possibility of adsorbed CO on the solid surface. Samples of **7**, which were prepared in different solvents (toluene, hexane), showed the same IR spectra, which was also obtained when solid **6** was stored under CO atmosphere. We finally obtained single crystals of **7** by treating a saturated solution of **6** in hexane with CO and storage at -30 °C for 24h. The X-ray analysis proved the presence of two independent molecules in the asymmetric unit, from which one (**7b**) shows weak intermolecular interactions between CO and fluorine atoms of the C₆F₅ rings of the second molecule (**7a**). The donation of electron density from the nonbonding *p*-orbitals (F) into the antibonding π^* -orbital (CO) weakens the CO bond, hence the bands at 2122 cm⁻¹ and 2135 cm⁻¹ are assigned to **7b** and **7a**.

Scheme 8. Copper carbonyl complexes synthesized by Sadighi *et al.*^[9]

The electronic properties of **7** were further compared to Cu(CO) complexes (scheme 8).^[9] Sadighi *et al.* reported that CF₃-substitution in the ligand backbone has a greater electronic effect on the CO stretching band than CF₃-substitution in meta-position of the aryl rings. While replacement of the Me groups (**8d**) by CF₃ groups in the ligand backbone (**8b**) resulted in a shift of the CO stretching band by 24 cm⁻¹, the introduction of meta-CF₃-groups (**8c**) shifted the CO stretching band by 17 cm⁻¹. **8a**, in which both effects are combined, showed the largest shift (27 cm⁻¹) of the CO stretching band to 2100 cm⁻¹. Replacement of the 3,5-(CF₃)₂-C₆H₃ substituents in **8a** by C₆F₅ groups in **7** now shifts the CO stretching band by 38 cm⁻¹ (from 2097 cm⁻¹ to 2135 cm⁻¹), proving the drastically reduced π -back-bonding capacity of the Cu atom.

Table 1. CO stretching bands in β -diketiminate Cu complexes.^[9]

	8a	8b	8c	8d
$\nu(\text{CO})$	2100	2097	2090	2073

Solid state Structures. **1** (Fig. 1) and **2** (Fig. S32) crystallize in the triclinic space group *P*-1 and *P*2₁/*n*, and **3** (Fig. S33) in the orthorhombic space group *Pbca*. **1** adopts a planar configuration with the C₆F₅ rings standing perpendicular to the ligand core.

Figure 1. Molecular structure of LH in the crystal of **1**. Displacement ellipsoids are drawn at the 50% probability level.

The introduction of CF₃ groups in **1** leads to an elongation of the C1-C4 (1.5233(14) Å) and C3-C5 (1.5335(14) Å) bond lengths compared to β -diketimines HC[C(CH₃)N(Ar)]₂ bearing CH₃ groups (Ar = 2,6-Me₂C₆H₃)₂ (dmpH); C₆F₅)₂ (pfpH)),^[8e,18] whose steric demand is comparable to that of **1** (table 2).

Table 2. Selected bond lengths [Å] and angles [°] of β -diketimines HC[C(CH₃)N(C₆F₅)₂H] (pfpH), HC[C(CH₃)N(C₆H₅)₂H] (dpH) and HC[C(CH₃)N(2,6-Me₂C₆H₃)₂H] (dmpH) with **1**.

	pfpH ^[a]	dpH ^[a]	dmpH ^[a]	1
C1-C2	1.358(3), 1.385	1.352(8)	1.371(6)	1.3603(13)
C1-C4	1.497, 1.493	1.499(8)	1.497(6)	1.5233(14)
C2-C3	1.438(3), 1.408	1.447(8)	1.425(6)	1.4389(14)
C3-C5	1.503, 1.506	1.540(8)	1.506(6)	1.5335(14)
N1-C1	1.361(3), 1.347	1.376(8)	1.336(5)	1.3588(13)
N2-C3	1.300(3), 1.320	1.314(8)	1.300(5)	1.2895(13)
C2-C3-C5	117.4, 117.1	117.2(5)	118.0(4)	116.5(1)
C2-C1-C4	121.2, 119.6	118.4(5)	121.5(4)	118.4(1)
C1-C2-C3	125.8(2), 127.6	126.8(1)	125.3(4)	123.3(1)
N1-C1-C2	120.4(2)	121.1(1)	120.5(4)	124.8(1)
N2-C3-C2	119.5(2)	118.8(5)	119.8(4)	121.8(1)

[a] Values without s.u. were calculated from the deposited data.^[8e,18]

In addition, the C2-C1-C4 (118.37(9)°) and C2-C3-C5 (116.46(9)°) bond angles of **1** are smaller. The structural parameters indicate a higher *p*-orbital character in the C-CF₃-bonds, in agreement with Bent's rule.^[17] The C1-C2-C3 bond angle in **1** (123.26(9)°) is slightly diminished and the endocyclic

N1-C1-C2 (124.78(9)°) and N2-C3-C2 (121.78(9)°) bond angles are widened. The N2-C3 bond (1.2895(13) Å) in **1** is shorter than the N1-C1 bond (1.3588(13) Å), proving the higher π -bonding contribution. The short C-N and C-C bond lengths indicate a delocalized π -electron system. Compared to other β -diketimines, the shortening of the N2-C3 bond agrees with the electron deficient nature of the carbon atoms of the ligand backbone.

4 crystallizes in the monoclinic space group $P2_1/c$ with two independent molecules in the asymmetric unit (Fig. 2), whereas **5** crystallizes in the triclinic space group $P-1$ (Fig. 3).

Figure 2. Molecular structure of LAIme₂ in the crystal of **4**. The second independent molecule of the asymmetric unit is omitted but shows a similar conformation. Displacement ellipsoids are drawn at the 50% probability level.

Figure 3. Molecular structure of LZnEt in the crystal of **5**. Displacement ellipsoids are drawn at the 50% probability level.

The C_3N_2M rings are almost planar (deviation from planarity 0.189(3) Å / 0.045(3) Å **4**; 0.0109(14) Å **5**) and the C_6F_5 groups adopt perpendicular orientations, thus any mesomeric effect (-M effect) on the β -diketiminate π -system ($C_{\text{backbone}}-N-C_{\text{ipso}}-C_{\text{ortho}}$ 95.5(3)°, 92.8(3)° / 89.3(3)°, 92.5(8)°) can be excluded. The structure of **5** is comparable ($C_{\text{backbone}}-N-C_{\text{ipso}}-C_{\text{ortho}}$ 95.5(3)°, 92.8(3)° / 89.3(3)°, 92.5(8)°), only the C_6F_5 groups are slightly more tilted, indicating stronger repulsive interaction with the Et group (**5**) than with the smaller Me groups (**4**).

Table 3. Comparison of selected bond lengths [Å] and angles [°] of **4** and **5**.

	4	5
C1-C2	1.391(3), 1.398(3)	1.3961(15)
C1-C4	1.534(3), 1.583(9)	1.5329(15)
N1-M	1.9482(18), 1.938(2)	2.0030(9)
N2-M	1.9426(18), 1.9347(17)	1.9920(9)
C1-C2-C3	125.36(18), 125.2(2)	126.67(10)
C1-C2-C4	116.39(17), 116.1(3)	116.13(10)
N1-M-N2	93.02(7), 93.13(8)	93.43(4)

[a] Values without s.u. were calculated from the deposited structure data.

5 shows a weak intramolecular $CH\cdots\pi$ interaction ($H\cdots$ centroid 3.37 Å; SI). The endocyclic C-C-N backbone angles (table 3) in **4** and **5** are larger and the exocyclic C-C- CF_3 bond angles smaller than expected for a sp^2 -hybridized carbon atom, indicating higher p-orbital character of the C- CF_3 bond. The larger steric demand of the CF_3 groups leads to slightly larger exocyclic C-N- C_{aryl} angles in **4** (122.09(17)°, 121.77(17)° / 122.67(19)°, 123.0(4)°) compared to Me-substituted β -diketiminate aluminum complexes (table S2). Metal-N bonds in **4** (1.9426(18) / 1.9482(18) Å) and **5** (1.9920(9) / 2.0030(9) Å) are slightly longer than the mean values reported in the Cambridge structural database for β -diketiminate aluminum and zinc complexes $HC[C(Me)NAr]_2MR_x$ ($MR_x = AlMe_2$ [4a,8e] 1.920 Å; $ZnEt$ 1.962 Å) [19] bearing Me groups and substituted aryl rings (Ph, dmp, Mes, Dipp). The structural findings indicate slightly weaker metal-N bonds in **4** and **5**, in agreement with the reduced electron density due to the presence of electron withdrawing CF_3 and C_6F_5 groups. In addition, the endocyclic N-M-N bond angles in **4** and **5** are more acute compared to non-fluorinated β -diketiminate complexes, which exceed 94° (LAIme₂ except for pfpAlMe₂ [4a]) and 95° (LZnEt). The structural findings confirm the reduced electron-donating properties of **1**.

Figure 4. Molecular structure of LCu(C_6H_6) in the crystal of **6**. H-atoms were omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

Figure 5. Molecular structure of **7**. H-atoms were omitted for clarity. The 2. independent molecule of the asymmetric unit is omitted but shows a similar conformation. Displacement ellipsoids are drawn at the 50% probability level.

6 (Fig. 4) and **7** (Fig. 5) crystallize in the monoclinic space groups $P2_1/m$ and $P2_1/c$ with the molecules placed on 2e and one C_6D_6 molecule on the same special position (**6**) or with two independent molecules in the asymmetric unit (**7**). The C_6F_5 groups adopt perpendicular orientations and the Cu atoms are almost in plane with the C_3N_2 unit (dev. from best plane 0.014(6) Å **6**, 0.1391(25) Å **7a** / 0.1311(24) Å **7b**). The Cu-N bond lengths of **6** (1.9540(14) Å) agree with those of $L^*Cu(C_6D_6)$ (1.954(3) / 1.952(3) Å),^[9] while the N1-Cu1-N2 bond angle for **6** is slightly smaller (98.58(6)° vs 99.60(12)°). The C_6D_6 ring is η^2 -bonded (Cu1-C10 2.1226(14) Å) and the C10-C10a bond length (1.380(4)) identical to that in free benzene (1.380(13) Å),^[20] indicating weak π -back-bonding. Comparable values were reported for $L^*Cu(C_6D_6)$ (Cu-C 2.117(4) Å, 2.102(4) Å, C-C 1.385(6) Å, C-Cu-C 38.35(17)°).^[9]

The Cu-N bond lengths in **7** (av. 1.9426 Å, 1.9388 Å) are slightly shorter compared to **6** (1.9540 Å), whereas the N-Cu-N bond angles (98.58(6)° **6**; 97.18(7)° and 98.66(7)° **7**) are comparable (table 4). The Cu-C-O unit in **7a** is almost linear (179.3(3)°), while that in **7b** slightly deviates from linearity (175.2(2)°). In addition, **7b** shows five close contacts to fluorine atoms of adjacent C_6F_5 rings (shortest: O1-F13 2.679(3) Å), which are within the sum of the van der Waals radii (2.99 Å).^[21] The slightly smaller Cu-C-O angle in combination with short intermolecular contacts indicate an interaction of the fluorine atoms with the π -system (Fig. 6).

Figure 6. Intramolecular interaction of the CO ligand of **7b**. H-atoms and non-interacting F-atoms of the symmetry generated molecules were omitted for clarity. Symmetry generated molecules are displayed in pale colors. Atoms are displayed as spheres of arbitrary size.

Table 4. Selected bond lengths [Å] and angles [°] of **6** and the two independent molecules of the asymmetric unit in the crystal of **7**.

	6	7a	7b
Cu1-C	2.1226(14), 2.1226(14)	1.809(3)	1.806(2)
Cu1-N1/2	1.9540(10), 1.9539(10)	1.9403(17), 1.9449(17)	1.9373(16), 1.9403(16)
C10-C10a	1.380(4)	-	-
C18-O1	-	1.118(3)	1.121(3)
N1-Cu1-N2	98.58(6)	97.18(7)	98.66(7)
C10-Cu1-C10a	37.93(10)	-	-
Cu1-C10-C10a	71.03(5)	-	-
Cu1-C10-C11	105.13(11)	-	-
Cu1-C18-O1	-	179.3(3)	175.2(2)

[a]

To further investigate the fluorine- π -interactions as-observed in the crystal structure of **7b**, quantum chemical calculations were performed on the B3LYP/6-31(d,p) level. The model used for calculation was derived from the crystal structure of **7**, replacing two of the interacting $C_6F_5[NC(CF_3)CHC(CF_3)NC_6F_5]$ units with simple C_6F_6 groups at the same location. Figure 7 shows the resulting NBOs. All fluorine lone pairs, which interact with the CO group, populate antibonding π_{CO}^* orbitals, thus strongly supporting the hypothesis given in the discussion of the IR spectra.

Figure 7. NBOs for the interaction of two C_6F_6 molecules with the CO ligand of **7b** at an isovalue of 0.02.

Conclusions

The synthesis and solid state structure of the fluorinated β -diketimine **LH 1** ($L = HC[C(CF_3)N(C_6F_5)]_2$) is reported and its capability to serve as N,N' -chelating substituent in main group metal and transition metal chemistry is demonstrated. In addition to the electron withdrawing CF_3 groups in the ligand backbone, the C_6F_5 groups bound to the imine centers also have a strong effect on the electronic properties of the ligand as was demonstrated for the carbonyl complex **LCuCO 7**. The absorption band of the CO stretching vibration in the IR spectrum of **7** is shifted by 38 cm^{-1} compared to the comparable copper complex **8a** bearing a 3,5- $(CF_3)_2-C_6H_3$ substituents at the nitrogen centers. This finding proves the drastically reduced π -back-bonding capacity of the electron-deficient copper atom in **7**. The high steric demand combined with the less electron-donating properties may

help to stabilize low-valent metal centers such as $Zn(I)$ or $Al(I)$ complexes in the future.

Experimental Section

General procedures: All reactions were performed under purified argon atmosphere using standard Schlenk and glovebox techniques. Solvents were dried over activated alumina columns using an MBraun Solvent Purification System (toluene, *n*-hexane) or distilled over potassium (benzene) and degassed prior to use. All solvents were stored over activated molecular sieves (*n*-hexane 3Å, toluene and benzene 4 Å). Solvents for column chromatography were bought as p.a.-grade and used as received. Deuterated NMR solvents were stored over activated molecular sieves (4 Å) and degassed prior to use. Karl Fischer titration of the dry solvents showed values less than 2 ppm. Exact molar ratios of the reactions and reaction conditions were optimized by monitoring several small-scale reactions, which were performed in *J-Young* NMR tubes in deuterated solvents under different reaction conditions, by *in situ* 1H -NMR spectroscopy.

Instrumentation: 1H (300 and 500 MHz), $^{13}C\{^1H\}$ (75.5 and 150 MHz) and $^{13}C\{^{19}F\}$ (75.5 and 150 MHz) NMR (δ in ppm) spectra were recorded either using a Bruker Avance DPX-300, a Bruker Avance III HD or a Bruker Avance HD600 spectrometer. Spectra were referenced to internal C_6D_5H (1H : $\delta = 7.154$; ^{13}C : $\delta = 128.39$), $C_6D_5CHD_2$ (1H : $\delta = 2.09$; ^{13}C : $\delta = 20.40$), $CHCl_3$ (1H : $\delta = 7.26$, ^{13}C : $\delta = 77.16$) and $CDHCl_2$ (1H : $\delta = 5.32$, ^{13}C : $\delta = 53.84$). Microanalyses were performed at the Elemental Analysis Laboratory of the University of Duisburg-Essen. IR spectra were measured with an ALPHA-TFT-IR spectrometer equipped with a single reflection ATR sampling module. Melting points were measured using a Thermo Scientific 9300 apparatus and are not corrected.

Synthesis of LH 1: A solution of $TiCl_4$ (3.19 g, 1.84 mL, 16.8 mmol) in 50 mL of *n*-hexane was added dropwise at $0^\circ C$ to a solution of $C_6F_5NH_2$ (9.93 g, 54.6 mmol) in 150 mL of *n*-hexane. The reaction mixture was heated under reflux for 2 h and then combined with 1,1,1,5,5,5-hexafluoroacetylacetone (1.31 g, 0.86 mL, 6.3 mmol). The resulting suspension was heated under reflux for further 16 h, treated with sodium bicarbonate solution, filtered and washed with sodium bicarbonate solution and brine. The organic layers were reduced in vacuo and the resulting oily residue was purified via two different column chromatography cycles (*n*-hexane / ethyl acetate 19:1 followed by cyclohexane / dichloromethane 24:1). After removing the solvent, **1** was obtained as a bright yellow solid.

$HC[C(CF_3)NC_6F_5]_2H$ 1: Yield: 1.285 g (38 %) M.p. $69^\circ C$. Elemental analysis calcd. (found) for $C_{17}H_2F_{16}N_2$ (538.19 g/mol): C, 37.94 (38.10); H, 0.37 (0.33); N, 5.21 (5.49). 1H NMR (300 MHz, CD_2Cl_2): δ 10.99 (s, 1H, NH), 6.18 (s, 1H, γ -CH). $^{13}C\{^1H\}$ NMR (300 MHz, CD_2Cl_2): δ 154.7 (q, $^3J_{CF} = 31.8\text{ Hz}$, *ortho*- C_{Ar}), 142.0 (m, *para*- C_{Ar}), 139.9 (m, *meta*- C_{Ar}), 136.8 (m, *ipso*- C_{Ar}), 118.9 (q, $^1J_{CF} = 282.6\text{ Hz}$, C_6F_5), 117.6 (td, $^2J_{CF} = 17.9\text{ Hz}$, C_6F_5), 92.2 (t, $^3J_{CF} = 4.31\text{ Hz}$, γ -CH). $^{13}C\{^{19}F\}$ NMR (300 MHz, CD_2Cl_2): δ 154.7 (s, *ortho*- C_{Ar}), 142.0 (m, *para*- C_{Ar}), 139.9 (s, *meta*- C_{Ar}), 136.8 (s, *ipso*- C_{Ar}), 117.6 (s, C_6F_5), 92.2 (d, $^1J_{CH} = 171.0\text{ Hz}$, γ -CH). ^{19}F NMR (300 MHz, CD_2Cl_2): δ -68.3 (t, $^6J_{FF} = 4.4\text{ Hz}$, 6F, C_6F_5), -147.9 (dt, $^3J_{FF} = 20.9\text{ Hz}$, $^4J_{FF} = 4.1\text{ Hz}$, 4F, *ortho*-F), -156.9 (t, $^3J_{FF} = 21.3\text{ Hz}$, 2F, *para*-F), -162.8 (td, $^3J_{FF} = 21.5\text{ Hz}$, $^4J_{FF} = 5.3\text{ Hz}$, 4F, *meta*-F). IR (ATR): ν 3134 (w), 1658 (m), 1581 (s), 1504 (s), 1456 (m), 1382 (m), 1332 (m), 1311 (m), 1274 (m), 1191 (s), 1148 (s), 1095 (s), 1018 (m), 911 (s), 856 (s), 804 (s), 765 (w), 717 (m), 694 (m).

2 was isolated as a colorless solid from the second fraction of the second column chromatography cycle.

HC[C(CF₃)NC₆F₅]COCF₃H **2**: Yield: 0.45 g (14 %). M.p. 118 °C. Elemental analysis calcd. (found) for C₁₁H₂F₁₁NO (373.13 g/mol): C, 34.27 (34.00); H, 0.54 (0.52); N, 3.65 (3.60). ¹H NMR (300 MHz, CD₂Cl₂): δ 10.70 (br s, 1H, NH), 6.25 (s, 1H, γ-CH). ¹³C{¹⁹F} NMR (300 MHz, CD₂Cl₂): δ 182.3 (s, (CF₃)CO), 153.1 (s, (CF₃)CN) 145.5 (s, C_{Ar}), 145.3 (s, C_{Ar}), 142.7 (s, C_{Ar}), 142.6 (s, C_{Ar}), 138.4 (s, C_{Ar}), 138.1 (s, C_{Ar}), 111.9 (s, (CF₃)CN), 91.8 (d, ¹J_{CH} = 173.0 Hz). ¹⁹F NMR (282 MHz, CD₂Cl₂): δ -68.5 (t, ⁶J_{FF} = 5.0 Hz, 3F, CF₃), -78.5 (s, 3F, CF₃), -144.5 (m, 2F, *ortho*-F), -152.0 (td, ³J_{FF} = 21.3 Hz, ⁴J_{FF} = 1.8 Hz, 1H, *para*-F), -161.9 (m, 2F, *meta*-F). IR (ATR): ν 3179 (w), 1613 (m), 1510 (s), 1372 (m), 1264 (m), 1207 (s), 1133 (s), 1089 (s), 1015 (s), 989 (s), 886 (m), 808 (s), 732 (m), 643 (s), 581 (s), 544 (m).

Synthesis of 2 via Aza-Wittig reaction: Ph₃P=NC₆F₅ was synthesized according to a literature procedure.^[22] Ph₃P=NC₆F₅ (35 mg, 78 μmol) was dissolved in 0.7 mL of toluene-d₈ in a *J-Young* NMR tube and treated with fac₂H (8.21 mg, 5 μL, 39 μmol). After heating to 105 °C for 12 h, fac₂H was totally consumed. The solution was treated with sodium bicarbonate solution, filtered and washed with sodium bicarbonate solution. The organic layers were reduced *in vacuo* and the resulting residue was purified via micro column chromatography (*n*-hexane / ethyl acetate 19:1). After removing of the solvent, **2** was obtained as a white solid in 75 % yield (10 mg).

Synthesis of 3: TiCl₄ (0.55 g, 0.32 mL, 2.9 mmol) was added dropwise to a solution of C₆F₅NH₂ (0.55 g, 2.9 mmol) and Et₃N (0.68 g, 0.93 mL, 6.7 mmol) in 20 mL of hexane at 0 °C. The mixture was heated under reflux for 2 h and then combined with 1,1,1,5,5,5-hexafluoroacetylacetone (0.20 g, 0.13 mL, 1.0 mmol), yielding a suspension that was heated under reflux for additional 16 h, treated with sodium bicarbonate solution, filtered and washed with sodium bicarbonate solution and brine. The solvent of the organic layers was removed *in vacuo* and the oily residue was purified via two different column chromatography cycles (*n*-hexane / ethyl acetate 19:1 followed by cyclohexane / dichloromethane 24:1). After removing the solvents *in vacuo* compound **3** was obtained as an oil which solidified after 3 days of standing as a yellow solid.

HC[C(CF₃)NC₆F₄NC₆F₅C(CF₃)] **3**: Yield: 0.14 g (28 %). M.p. 68 °C. Elemental analysis calcd. (found) for C₁₇H₂F₁₅N₂ (518.19 g/mol): C, 34.37 (34.30); H, 0.19 (0.24); N, 3.41 (3.50). ¹H NMR (300 MHz, CD₂Cl₂): δ 6.75 (s, 1H, γ-CH). ¹³C{¹⁹F} NMR (300 MHz, CD₂Cl₂): δ 154.8 (N=C), 154.5 (N-C), 145.7 (C_{Ar}), 144.8 (C_{Ar}), 143.4 (C_{Ar}), 143.4 (C_{Ar}), 143.0 (C_{Ar}), 141.7 (C_{Ar}), 141.6 (C_{Ar}), 139.2 (C_{Ar}), 138.2 (C_{Ar}), 129.9 (C), 125.1 (C), 120.4 (N=CCF₃), 119.3 (N-CCF₃), 118.8 (C), 117.3 (C). ¹⁹F NMR (282 MHz, CD₂Cl₂): δ -70.4 (t, ⁶J_{FF} = 7.6 Hz, 3F, CF₃), 73.2 (s, 3F, CF₃), -140.1 (m, 2F, *meta*-C₆F₅), -142.6 (dd, ³J_{FF} = 21.1 Hz, ⁴J_{FF} = 8.4 Hz, 1F, *meta*-C₆F₄), -147.2 (m, 1F, *para*-C₆F₅), -151.5 (t, ³J_{FF} = 21.2 Hz, 1F *ortho/para*-C₆F₄), 151.8 (t, ³J_{FF} = 21.0 Hz, 1F, *para/ortho*-C₆F₄), -155.6 (t, ³J_{FF} = 20.7 Hz, 1F, *ortho*-C₆F₄), -161.6 (t, ³J_{FF} = 20.5 Hz, 2F, *ortho*-C₆F₅). IR (ATR): ν 2960 (w), 2920 (w) 2863 (w), 1668 (w), 1622 (w), 1491 (s), 1337 (w), 1274 (w), 1202 (s), 1138 (s), 1077 (m), 1040 (s), 991 (s), 884 (s), 843 (m), 785 (m), 766 (m), 725 (m), 683 (w), 657 (w), 623 (m), 467 (w).

Synthesis of LAIme₂ 4: A solution of **1** (0.15 g, 0.3 mmol) in 10 mL of *n*-hexane was cooled to -78 °C and treated with a solution of Me₃Al (0.22 mL, 0.16 g, 1.1 mmol). The resulting yellow solution was stirred for 10 minutes at -78 °C, slowly warmed to ambient temperature and stirred for additional 30 minutes. After all volatiles were removed *in vacuo*, the resulting remaining yellow solid was recrystallized from a solution in *n*-hexane, yielding of **4** as bright yellow, prismatic crystals.

LAIme₂ **4**: Yield: 0.15 g (88 %). M.p. 74.6 °C. Elemental analysis calcd. (found) for C₁₉H₇AlF₁₆N₂ (594.23 g/mol): C, 38.40 (38.21); H, 1.19 (1.16); N, 4.71 (4.70). ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ 6.34 (s, 1H, γ-CH), -0.91 (s, 6H, Al(CH₃)₂). ¹³C{¹H} NMR (300 MHz, CDCl₃): δ 161.0 (q, ²J_{CF} =

31.0 Hz, *ortho*-C_{Ar}), 142.7 (q, ¹J_{CF} = 127.7 Hz, *para*-C_{Ar}), 139.5 (m, *meta*-C_{Ar}), 136.5 (t, ³J_{CF} = 15.1 Hz, *ipso*-C_{Ar}), 117.2 (q, ³J_{CF} = 286.5 Hz, C₆F₃), 92.6 (s, γ-CH), -12.6 (s, Al(CH₃)₂). ¹³C{¹⁹F} NMR (300 MHz, CDCl₃): δ 161.0 (s, *ortho*-C_{Ar}), 142.7 (s, *para*-C_{Ar}), 139.5 (s, *meta*-C_{Ar}), 136.5 (s, *ipso*-C_{Ar}), 117.2 (s, C₆F₃), 92.6 (d, ²J_{CH} = 172.0 Hz, γ-CH), -12.6 (q, ²J_{CH} = 115.7 Hz, Al(CH₃)₂). ¹⁹F NMR (300 MHz, CDCl₃) δ [ppm]: -66.9 (t, ⁶J_{FF} = 4.5 Hz, 6F, C₆F₃), -145.5 (d, ¹J_{CF} = 20.6 Hz, 4F, *ortho*-F), -153.3 (t, ¹J_{CF} = 21.3 Hz, 2F, *para*-F), -160.7 (td, ¹J_{CF} = 20.3 Hz, 4F, *meta*-F). ²⁷Al NMR (300 MHz, CD₃Cl) δ [ppm]: 168.9 (s). IR (ATR): ν 2962 (w), 1578 (m), 1508 (s), 1461 (s), 1415 (s), 1343 (s), 1318 (w), 1288 (w), 1260 (m), 1197 (m), 1146 (s), 1093 (s), 1054 (s), 1027 (s), 989 (s), 875 (w), 787 (s), 692 (s), 630 (s).

Synthesis of LZnEt 5: A solution of **1** (0.11 g, 0.2 mmol) in 10 mL of *n*-hexane was treated with a 1M solution of Et₂Zn (0.40 mL, 0.4 mmol) at -78 °C. After warming to room temperature within 2 h, the yellow solution was stirred for additional 30 minutes and all volatiles were removed *in vacuo*. The resulting bright yellow solid was recrystallized from a solution in *n*-hexane, yielding two crops of **4** as bright yellow needles.

LZnEt **5**: Yield: 0.20 g (85%). M.p. 102.3 °C. Elemental analysis calcd. (found) for C₁₉H₆F₁₆N₂Zn (%) C 36.13 (35.7), H 0.96 (0.878), N 4.44 (4.43). ¹H NMR (300 MHz, CDCl₃): δ 6.22 (s, 1H, γ-CH), 0.74 (t, ³J_{HH} = 8.1 Hz, 3H, ZnCH₂CH₃), 0.11 (q, ³J_{HH} = 8.1 Hz, 2H, ZnCH₂CH₃). ¹³C{¹H} NMR (300 MHz, CDCl₃): δ 160.0 (d, ²J_{CF} = 29.0 Hz, C_{Ar}), 139.1 (br m, C_{Ar}), 118.9 (q, ¹J_{CF} = 285.2 Hz, C₆F₃), 89.5 (q, ³J_{CF} = 9.7 Hz, γ-CH), 11.0 (s, ZnCH₂CH₃), 1.2 (s, ZnCH₂CH₃). ¹³C{¹⁹F} NMR (300 MHz, CDCl₃): δ 160.0 (s, C_{Ar}), 140.1 (br m, C_{Ar}), 139.5 (s, C_{Ar}), 136.4 (s, C_{Ar}), 121.3 (s, C₆F₃), 90.5 (s, γ-CH), 13.5 (s, ZnCH₂CH₃), 0.4 (s, ZnCH₂CH₃). ¹⁹F NMR (300 MHz, CDCl₃) δ [ppm]: -66.4 (t, ⁶J_{FF} = 5.2 Hz, 6F, C₆F₃), -147.2 (m, 4F, *ortho*-F), -156.0 (t, ³J_{FF} = 21.4 Hz, 2F, *para*-F), -161.5 (m, 4F, *meta*-F). IR (ATR), ν [cm⁻¹]: 2256 (s), 2872 (s), 1569 (m), 1506 (s), 1464 (s), 1417 (s), 1281 (m), 1196 (s), 1153 (s), 986 (s), 803 (m), 558 (m).

Synthesis of LCu(C₆D₆) 6: MesCu (0.3 g, 0.2 mmol) was dissolved in 0.7 mL of benzene-d₆ in a *J-Young* NMR tube and treated with a solution of **1** (0.10 g, 0.2 mmol) in 0.3 mL benzene-d₆ at room temperature. The yellow solution turned red within 20 minutes and was stirred for additional 12 h. Removing solvent and washing with cold hexane (-20 °C) followed by drying *in vacuo* gave **6** as a bright orange solid.

HC[C(CF₃)NC₆F₅]₂Cu(C₆D₆) **6**: Yield 0.7 g (53 %). M.p. 107 °C (decomp.). Elemental analysis calcd. (found) for C₄₀H₈CuF₂N₄ (1277.88 g/mol): C 37.55 (37.37) H 0.63 (0.59), N 4.38 (4.45). ¹H NMR (300 MHz, C₆D₆): δ 5.87 (s, 1H, γ-CH). ¹³C{¹⁹F} NMR (300 MHz, C₆D₆): 156.2 (s, C_{Ar}), 141.5 (s, C_{Ar}), 140.5 (s, C_{Ar}), 138.2 (s, C_{Ar}), 138.2 (s, C_{Ar}), 138.1 (s, C_{Ar}), 124.0 (s, C_{Ar}), 119.9 (s, C_{Ar}), 87.0 (d, ¹J_{CH} = 165.1 Hz γ-CH). ¹⁹F NMR (282 MHz, C₆D₆): -66.1 (t, ⁶J_{FF} = 4.1 Hz, 6F, CF₃), -148.8 (m, 4F, *ortho*-F), -159.2 (t, ³J_{FF} = 22.6 Hz, 2F, *para*-F), -163.4 (td, ³J_{FF} = 23.6 Hz, ⁴J_{FF} = 6.2 Hz, 4F, *meta*-F). IR (ATR): ν 2963 (w), 1564 (m), 1504 (s), 1464 (s), 1427 (s), 1323 (m), 1189 (s), 1138 (s), 983 (s), 802 (s), 521 (m).

Synthesis of LCu(CO) 7: A solution of **6** (0.4 g, 0.3 mmol) in 0.7 mL of benzene-d₆ in a *J-Young* NMR tube was frozen in liquid nitrogen, evacuated at 10⁻³ mbar and then refilled with one atmosphere of CO gas. Warming the mixture to ambient temperature resulted in the precipitation of the yellow complex LCuCO **7**, which was isolated by centrifugation and filtration. Single crystals of **7** were obtained upon treatment of a saturated solution of **6** in hexane with CO and storage at -30 °C for 24 h.

HC[C(CF₃)NC₆F₅]₂Cu(CO) **7**: Yield 0.37 g (68 %). ¹H NMR (300 MHz, C₆D₆): δ 5.97 (s, 1H, γ-CH). ¹⁹F NMR (282 MHz, C₆D₆): δ -65.6 (t, ⁶J_{FF} = 5.2 Hz, 6F, CF₃), -148.6 (m, 4F, *ortho*-F), -157.8 (t, ³J_{FF} = 22.1 Hz, 2F, *para*-F), -162.5 (dt, ³J_{FF} = 23.1 Hz, ⁴J_{FF} = 6.3 Hz, 4F, *meta*-F). IR (ATR):

2135 (s), 2122 (s), 1505 (s), 1462 (s) 1420 (s), 1317 (m), 1286 (m), 1187 (s), 1139 (s), 1103 (m), 984 (s), 804 (m), 568 (w).

Single crystal X-ray diffraction. The crystals were mounted on nylon loops in inert oil. Data were collected on a Bruker AXS D8 Kappa diffractometer with APEX2 detector (mono-chromated MoK α radiation, λ = 0.71073 Å) at 100(2) K except for **6** with was measured at 200(2) K. The data of **2** were collected on a Rigaku Oxford Diffraction Xcalibur Nova diffractometer with Atlas detector (mono-chromated CuK α radiation, λ = 1.54184 Å) at 100(2). All structures were solved by Direct Methods (SHELXS-97)^[23] and refined anisotropically by full-matrix least-squares on F^2 (SHELXL-2014).^[24,25] Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2, CrysAlisPro). Hydrogen atoms were refined using a riding model or rigid methyl groups. In **1** and **2** the NH hydrogen atoms were refined freely. In **3** the CF₃ group of C5 is disordered over several positions of which the three largest could be modelled with the help of several restraints (SADI, RIGU, ISOR). Only the largest one could be refined anisotropically. In **4** one of each of the fluorinated groups of residue 1 is disordered. The disorder was modelled by two components yet the ADPs of the atoms indicate that this is only a moderate description, but no further components could be identified. RIGU restraints were employed to improve the refinement. Cooling the crystals of **6** to 100 K led to a serious loss of crystal quality. In this structure for the refinement of the ADP of both the free and coordinated benzene molecule rigid bond restraints (RIGU) were used. The solvent molecule is disordered over two positions.

CCDC 1833502-1833508 contain the 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.

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FULL PAPER

Aluminum, zinc and copper complexes of fluorinated β -diketimine LH **1** ($L = \text{HC}[\text{C}(\text{CF}_3)\text{N}(\text{C}_6\text{F}_5)]_2$) were synthesized and structurally characterized. The influence of the electron-withdrawing ligand on the π -back-bonding of the metal atom was shown for the copper carbonyl complex LCuCO **7**.

Fluorinated β -diketimine

*Kevin Huse, Christoph Wölper, Stephan Schulz**

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Main group metal and transition metal complexes containing fluorinated β -diketiminato ligands

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