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New Binding Modes of 1-Acetyl- and 1-Benzoyl-5-hydroxypyrazolines – Synthesis and Characterization of *O,O′*-Pyrazoline- and *N,O*-Pyrazoline-Zinc Complexes

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The 1-acetyl- and 1-benzoyl-5-hydroxypyrazolines **1a** [3,5-CF_3, 1-C(=O)CH_3], **1b** [3,5-CH_3, 1-C(=O)CH_3] and **1c** [3,5-CF_3, 1-C(=O)C_6H_5] have been synthesized in good yields and characterized by X-ray crystallography. The 1-acetyl- and 1-benzoyl-5-hydroxypyrazoline ligands were treated with dimethylzinc in a 1:1 molar ratio to form complexes **8** with a RO–Zn–Me motif. These complexes are accessible by simple Brønsted acid–base reactions generating methane as a side product. Characterization of complexes **8a** and **8c** by X-ray crystallography revealed a dimeric structure in the solid state. The two subunits generate a Zn_2O_2 square. The acetyl and benzoyl functionality of the ligands coordinate to the metal to span a six-membered ring. Moreover, the coordination mode of the ligand can be easily influenced by the addition of base. Here, *N,N,N′,N′*-tetramethylethylenediamine (tmeda) was applied to remove the acidic proton in the 4-position of the ligand and to cleave the hemiaminal functional group. The tmeda-H^+ transfers the proton to the methyl group connected to the zinc and facilitates the removal of methane; the free tmeda coordinates to the zinc in a bidentate fashion. The positive charge at the zinc and the negative charge in the ligand recombine to form complex **9**. Surprisingly, the characterization of complex **9c** by X-ray crystallography showed the formation of the first zinc-based seven-membered system with covalent bonding (N^1,O^6-coordination) in the solid state, whereas for other metals O^6,N^2,O^7-coordination has been reported.

Introduction

The development of sustainable, more efficient, and selective organic transformations remains a demanding task central for chemical synthesis in academia as well as in industry. In this regard, catalysis is a key technology since high atom efficiency, reduced amounts of waste and energy, and, as a consequence, advantageous economics are feasible.[1] In particular, molecular defined organometallic compounds have proven to be an excellent tool box as illustrated by the huge number of applications in organic chemistry.[2] The abilities of the catalyst are influenced by the selection of the central metal and by the design of surrounding ligands.[3] In particular, the choice of ligands coordinated to the transition metal center should be considered from chemical and economical points of view. Requirements for ligand technologies include cost efficiency, great availability, easy synthesis, high tunability, high flexibility and stability. Thus the design of new ligands and the study of their coordination chemistry is an important research goal.[4] With respect to these requirements, an interesting motif is the 5-hydroxypyrazoline ligand (**1**), which has different coordination possibilities (Figure 1). Due to tautomerism, various forms have been discussed, for example, the hydrazone and the corresponding enol, as well as enehydrazine form.[5] Attempts to coordinate **1** to metals, such as nickel, resulted in the formation of **2**; complexes containing one six- and one five-membered ring with the O^6,N^2,O^7-coordination mode (Figure 1).[5c] Only this motif has been structurally characterized by X-ray crystallography so far. Due to the binding diversity of the 5-hydroxypyrazoline ligands, we wondered if other structural motifs, such as **3** and **4** (tautomer of **2**), are feasible. As a metal that allows flexible coordination geometries, zinc has been reported by various research groups, but until now no pyrazoline–zinc complexes have been studied.[6]

Based on our ongoing studies in zinc chemistry, we herein report the synthesis and characterization of 5-hydroxypyrazoline zinc complexes by reacting cyclic 5-hydroxypyrazoline ligands with dimethylzinc.[7] Depending on the reaction conditions, different coordination modes were accessible. In the presence of *N,N,N′,N′*-tetramethylethylenediamine (tmeda) as deprotonation reagent, a N^1,O^6-binding mode was observed generating a seven-membered

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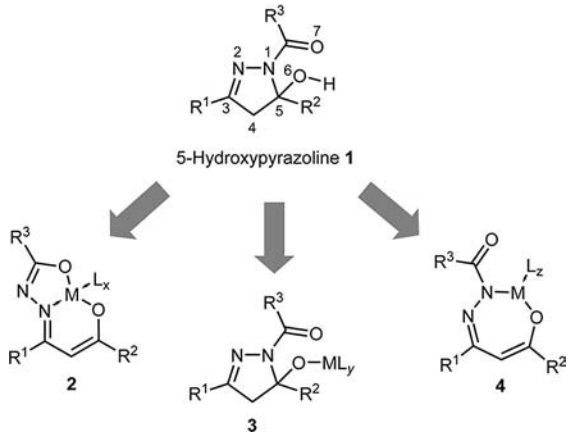


Figure 1. Coordination modes of 5-hydroxypyrazoline.

ring (**4**; Figure 1), whereas, in the absence of additional base, coordination to the 5-hydroxy functionality was observed (**3**; Figure 1).

Results and Discussion

Ligand Synthesis and Characterization

The ligands were prepared as outlined in Scheme 1. Acetohydrazide **6a** and benzohydrazide **6b** were synthesized by reacting equimolar amounts of hydrazine monohydrate with ethyl acetate or methyl benzoate, respectively, in ethanol under refluxing conditions.[5a] Both hydrazides were isolated in good yields as colorless solids. The hydrazides were treated with acetyl acetone **7a** or hexafluoroacetyl acetone **7b** under refluxing conditions to obtain pyrazolines **1a**–**c** in good yields (69–87%). The pyrazolines were purified either by crystallization from *n*-hexane or by high-vacuum sublimation. Surprisingly, the pyrazolines are quite stable since no elimination of water to form pyrazole derivatives was detected. In the case of compounds **1a**–**c**, crystals suitable for X-ray measurements were grown by the slow cooling of a saturated *n*-hexane solution. The reaction of **6b** and **7a** did not result in the desired product.

The solid-state structures of compounds **1a**–**c** have been characterized by single-crystal X-ray diffraction analysis. Thermal ellipsoid plots for the ligands are displayed in Figure 2 and selected bond lengths and angles are listed in Table 1. In agreement with earlier reports, the cyclic form was observed.[5c,5d] The bond length between the hydrogen atom of the hydroxy group [HO(2)] and the oxygen atom of acetyl group [O(1)] indicates that **1a** has an intramolecular hydrogen-bonding interaction with a distance of 2.381 Å (Figure 2, a); the same was observed in **1c** for which the intramolecular hydrogen-bonding distance was 2.158 Å (Figure 2, c). In case of **1b**, a dimeric structure was observed, in which an intermolecular hydrogen-bonding interaction is seen between the hydroxy group and the acetyl group of the neighboring molecule with a distance of 2.861 Å (Figure 2, b).

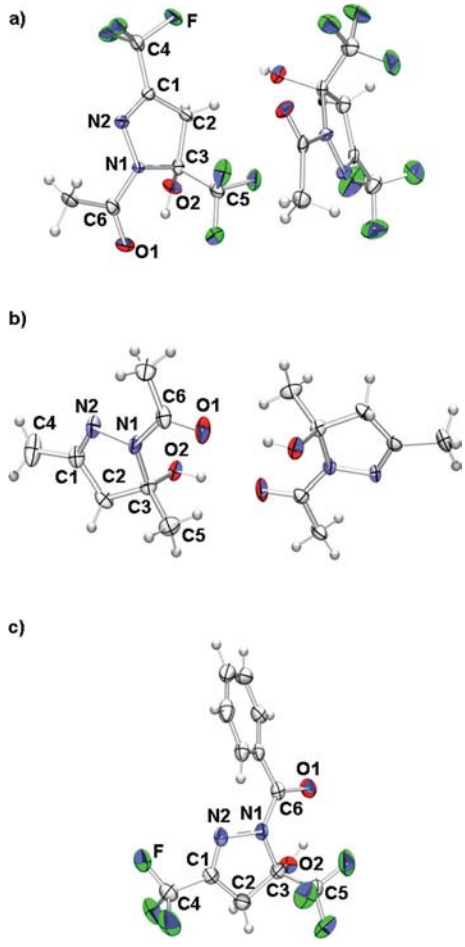
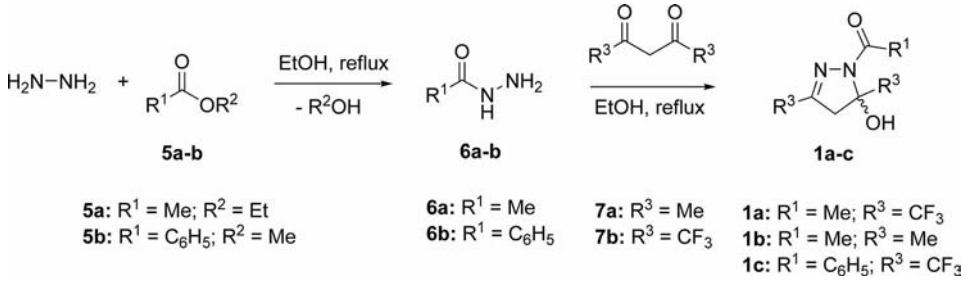


Figure 2. Molecular structure of **1a** (a), **1b** (b), and **1c** (c). Thermal ellipsoids are drawn at the 50% probability level.



Scheme 1. Synthesis of 1-acetyl- and 1-benzoyl-5-hydroxypyrazoline ligands **1**.

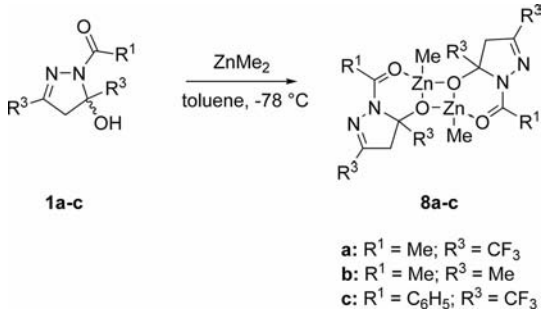
Table 1. Selected bond lengths [Å] of **1a**, **1b**, and **1c**.

	1a	1b	1c
N1–N2	1.396(4)	1.418(3)	1.396(2)
N1–C3	1.496(4)	1.493(4)	1.486(3)
N2–C1	1.263(4)	1.284(4)	1.271(3)
C2–C3	1.531(4)	1.487(4)	1.536(3)
C1–C2	1.487(4)	1.532(3)	1.487(3)
C1–C4	1.481(5)	1.521(3)	1.494(3)
C3–C5	1.536(4)	1.499(3)	1.540(3)
N1–C6	1.365(4)	1.367(3)	1.382(3)
C6–O1	1.221(4)	1.231(3)	1.224(2)
C3–O2	1.387(3)	1.420(3)	1.379(2)

With these suitable ligands in hand, we turned our attention to their coordination abilities towards zinc.

Synthesis and Characterization of the Zinc Complexes

In Scheme 2, the synthetic protocol to access pyrazoline–zinc complexes is given. The reaction of ligands **1a**–**c** with $ZnMe_2$ in a 1:1 ratio was carried out at low temperature (–78 °C) in toluene. After the evolution of methane, the reaction mixture was slowly warmed to room temperature and all volatiles were removed under vacuum to generate a powder, which was purified by crystallization giving colorless crystals.



Scheme 2. Synthesis of pyrazoline-zinc complexes **8a**–**c**.

For complexes **8a** and **8c** suitable crystals were obtained for single-crystal X-ray diffraction analysis. As shown in Figure 3, the zinc complexes exist in a dimeric form spanning a square planar Zn_2O_2 core with one pyrazoline above the plane and the other one underneath (*trans* positioned to each other). A similar structural motif has been recently reported in complexes of the type $[ArOZnMe]_2$ in which sterically hindered phenols are utilized as ligands.[7c] The selected bond lengths and angles around the zinc atoms in complexes **8a** and **8c** are listed in Table 2. These bond lengths are within the expected range based on previously reported four-membered Zn_2O_2 ring-containing complexes.[8] The acetyl and benzoyl functionality coordinates to the zinc atom (tetrahedral environment) from the top or bottom of the Zn_2O_2 plane, respectively. Interestingly, this motif can probably be seen as a potential intermediate (coordination and activation of the substrate) in the zinc-catalyzed reduction of amides or ketones.[7,9,10] The coordination of the acetyl and benzoyl functionality was investigated by IR spectroscopic measurements. A shift of 43 cm^{-1} was observed for **8a** [ν(C=O) 1655 cm^{-1}] compared with the free ligand **1a** [ν(C=O) 1698 cm^{-1}]. The complexes **8** were also characterized by ^1H NMR spectroscopy, which showed signals for Zn-CH_3 at δ = –0.44 (**8a**), –0.34 (**8b**) and –0.29 (**8c**) ppm. Furthermore, as expected the ^1H NMR signals for the hydroxy group disappeared on complexation. Experiments to confirm the presence of monomeric or dimeric species in solution or an equilibrium between these two forms have so far been unsuccessful, however, due to the use of non-coordinating solvents, such as C_6D_6, we assume a dimeric structure in solution.

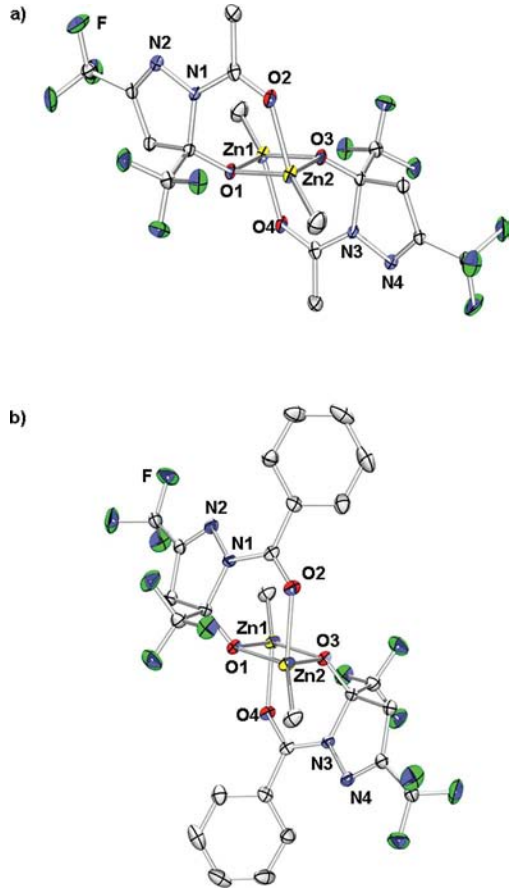


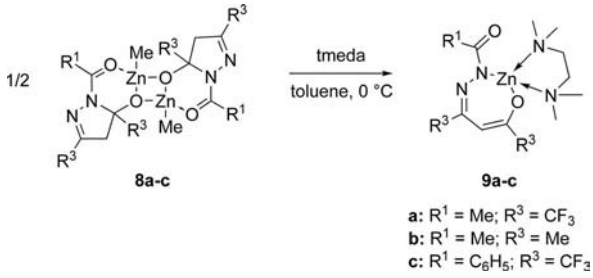
Figure 3. Molecular structure of **8a** (a) and **8c** (b). Thermal ellipsoids are drawn at the 50% probability level.

Table 2. Selected bond lengths [Å] for **8a** and **8c**.

	8a	8c
N1–N2	1.391(3)	1.399(3)
N1–C3	1.513(3)	1.524(3)
N2–C1	1.273(3)	1.274(3)
C2–C3	1.549(3)	1.547(3)
C1–C2	1.491(3)	1.489(3)
C1–C4	1.498(3)	1.491(3)
C3–C5	1.542(3)	1.530(3)
N1–C6	1.357(3)	1.364(3)
C6–O2	1.238(3)	1.247(3)
C3–O1	1.355(3)	1.355(3)

These complexes are the first examples in which 1-acetyl- and 1-benzoyl-5-hydroxypyrazolines coordinate in the O^6,O^7-fashion without the opening of the pyrazoline ring. Thus, we were interested in changing the coordination motif by opening the pyrazoline ring, which has been demonstrated for nickel complexes in the presence of base.[5c] Furthermore, labeling studies of the ligand in CD_3OD showed an exchange of one proton of the CH_2 group and, as a consequence, provided proof of the acidity of this functionality.

Complexes **8** were dissolved in toluene and cooled to 0 °C (Scheme 3). After the slow addition of 1 equiv. of tmeda all volatiles were removed under vacuum and the white residues were purified by crystallization. The reaction was followed by ^{1}H NMR spectroscopy and reached completion within one hour. During the reaction, the ^{1}H NMR signal for the Zn-CH_3 disappeared and the former CH_2 signal significantly shifted to lower field [δ = 2.87 (br., **8a**) compared with 5.79 (s; **9a**) ppm]; the integral area also reduced to only account for one proton. This corresponds to the deprotonation of the acidic CH_2 group by tmeda and transfer of the proton to the Zn-CH_3 to eliminate methane. The tmeda coordinates to the zinc ion, evidenced by shifts in the ^{1}H NMR signals compared with uncoordinated tmeda. Nevertheless, it is difficult to distinguish between the possible coordination modes of the ligand, such as O^6,N^1,O^7 as reported for nickel,[5c] by NMR spectroscopy. Fortunately, crystals suitable for single-crystal X-ray diffraction analysis were obtained for complex **9c**. The solid-state structure of **9c** revealed a new coordination mode of 1-acetyl- and 1-benzoyl-5-hydroxypyrazoline ligands with



Scheme 3. Reaction of complexes **8** with tmeda to form **9**.

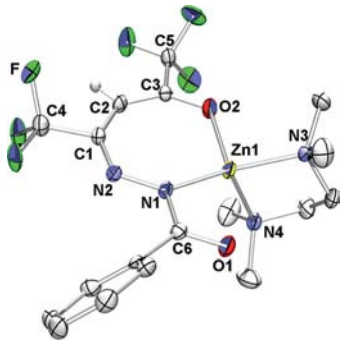


Figure 4. Molecular structure of **9c**. Thermal ellipsoids are drawn at the 50% probability level. Zn1–O2: 1.9462(15) Å; Zn1–N1: 1.9615(17) Å; Zn1–N3: 2.0710(17) Å; Zn1–N4: 2.0931(18) Å.

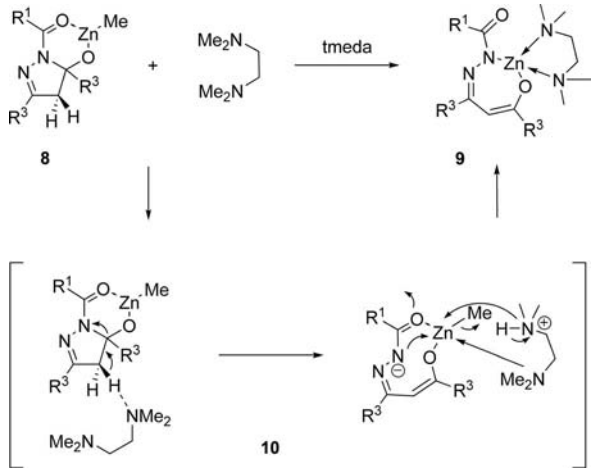
covalent bonds between the oxygen, nitrogen and the zinc atom forming the first zinc-containing seven-membered ring system (Figure 4).

Interestingly, the seven-membered ring is arranged in a plane and the tmeda ligand coordinates horizontally to this plane; the zinc atom has a tetrahedral coordination mode. The Zn1–O2 bond length (1.946 Å) bond is comparable to the distance observed for **8c** (Zn1–O1: 2.057 Å). The distance from the oxygen of the benzoyl group to the zinc atom is significantly longer (Zn1–O1: 2.611 Å) than that seen in **8c** (Zn1–O4: 2.078 Å). ^{19}F NMR spectroscopy was used as a probe to study the differences between compound **1c** and **9c** (Table 3); a significant shift to lower field was observed for one signal, which probably corresponds to the CF_3 group attached to the enolate motif. In the IR spectrum, differences in the position of the ν(C=O) peak, relative to that of **1c**, of 81 cm^{-1} for **8c** and 58 cm^{-1} for **9c** were observed.

Table 3. Comparison of selected properties of **1c**, **8c**, and **9c**.

	1c	8c	9c
^{1}H NMR 4-C*H*(*H*) [ppm]	3.00–3.66	2.94–3.15	5.79
^{19}F NMR [ppm]	–67.4; –80.5	–68.0; –82.1	–67.2; –71.6
IR ν(C=O) [cm^{-1}]	1680	1599	1622
C=N (Å)	1.271	1.277	1.287
C–C–O (Å)	1.536	1.547	1.345
N–C(=O) (Å)	1.382	1.363	1.355

Although the reaction mechanism for the formation of **9c** is unknown, a reasonable reaction mechanism is described in Scheme 4. The ring opening of the cyclic pyrazoline ligand **7** is initiated by the deprotonation of the acidic CH_2 functionality by tmeda to give the ring-opened intermediate **10**. The nine-membered ring-containing intermediate **10** undergoes intramolecular ligand substitution through nitrogen coordination to the zinc atom with the concomitant departure of the amide oxygen. The formation of compound **9** is completed by the elimination of methane gas and coordination of tmeda to the zinc center. This reaction mechanism was supported by theoretical calculations. DFT calculations were performed at B3LYP level using 6-



Scheme 4. Potential reaction pathway for the synthesis of **9**.

31G(d) basis set for C, N, O, F, and H atoms and LANL2DZ for the Zn atom with the GAUSSIAN-03 program package.[11] These calculation show that the formation of compound **9c** (and 2 equiv of methane) from compound **8c** with 2 equiv of tmeda is exothermal by 17.8 kcal mol^{-1}.

Conclusion

We have synthesized and characterized the first 5-hydroxypyrazoline zinc complexes with new coordination modes of pyrazolines, which demonstrate the modularity of pyrazoline ligands. The Brønsted acid–base reactions of dimethylzinc with 1-acetyl- and 1-benzoyl-5-hydroxypyrazoline resulted in the formation of [RO-Zn-Me]$_2$ complexes with a central Zn_2O_2 unit, which is stabilized by coordination of acetyl or benzoyl oxygens. Noteworthy, the pyrazoline ring is untouched. The addition of tmeda as base and ligand forces the opening of the pyrazoline ring at the hemiaminale position to form complexes with the O^6,N^1 coordination mode of the pyrazoline ligand. Here the first zinc-based seven-membered system with covalent bonding in the solid state has been observed. Future work will focus on the application of these complexes in catalysis.

Experimental Section

General: All manipulations with oxygen- and moisture-sensitive compounds were performed under N_2 using standard Schlenk techniques. Toluene and *n*-hexane were distilled from sodium/benzophenone ketyl under N_2. Dimethylzinc solution (1.2 M in toluene purchased from Aldrich) was used without further manipulation. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on a Bruker AFM 200 spectrometer (^{1}H: 200.13 MHz; ^{13}C: 50.32 MHz; ^{19}F: 188.31 MHz) using the proton signals of the deuterated solvents as reference. Single crystal X-ray diffraction measurements were recorded on an Oxford Diffraction Xcalibur S Saphire spectrometer. IR spectra were recorded on either a Nicolet Series II Magna-IR-System 750 FTR-IR or on a Perkin–Elmer Spectrum 100 FT-IR.

Acetohydrazide (6a):[12] Hydrazine monohydrate (0.20 mol) was added to a solution of ethyl acetate (0.19 mol) in ethanol (50 mL) at room temperature. After refluxing the mixture for 6 h the solvent was removed under vacuum and the colorless residue was dried under high vacuum; yield 10.3 g (87%, colorless crystals). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.07 (br., 1 H, NH), 3.80 (br., 2 H, NH_2), 1.88 (s, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 171.0, 20.6 ppm. IR (KBr): $\tilde{\nu}$ = 3292 (m), 1667 (s), 1528 (w), 1376 (w), 1311 (w), 1244 (m), 1157 (w), 993 (w) cm^{-1}.

Benzohydrazide (6b):[13] Hydrazine monohydrate (0.22 mol) was added to a solution of methyl benzoate (0.22 mol) in ethanol (50 mL) at room temperature. After refluxing the mixture for 6 h the solvent was reduced by half under vacuum. The colorless precipitate was filtered off, recrystallized from ethanol/*n*-hexane and dried under vacuum; yield 12.8 g (43%, colorless crystals). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 7.90 (br., 1 H, N*H*-NH_2), 7.72–7.81 (m, 3 H, C_6H_5), 7.37–7.56 (m, 2 H, C_6H_5), 4.13 (br., 2 H, NH-NH_2) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 168.7 (C=O), 132.6, 131.8, 128.6, 126.8 ppm. IR (KBr): $\tilde{\nu}$ = 3300 (m), 3020 (m), 3202 (m), 2879 (m), 1662 (m), 1616 (s), 1567 (m), 1350 (s), 1121 (m), 987 (m), 885 (m), 685 (s) cm^{-1}.

1-Acetyl-5-hydroxy-3,5-bis(trifluoromethyl)pyrazoline (1a): A solution of acetohydrazide (55.8 mmol) in ethanol (60 mL) was added to a solution of 1,1,1,5,5,5-hexafluoropeta-2,4-dione (**7b**, 55.8 mmol) in ethanol (60 mL). After refluxing the mixture for 5 h the solvent was removed under vacuum. The colorless residue was purified by recrystallization from *n*-hexane or by sublimation under high vacuum; yield 12.2 g (83%, colorless crystals). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 5.98 (br. s, 1 H, OH), 3.30–3.80 (m, 2 H, CH_2), 2.29 [s, 3 H, C(=O)CH_3] ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 173.3, 143.6 (m), 120.6 (m), 92.5 (m), 41.4 (CH_2), 22.4 (H_3CC=O) ppm. ^{19}F NMR (50 MHz, $CDCl_3$, 25 °C): δ = –67.8, –81.3 ppm. IR (KBr): $\tilde{\nu}$ = 2961 (w), 2933 (w), 2851 (w), 1655 (m), 1626 (s), 1466 (m), 1373 (m), 1344 (m), 1321 (m), 1282 (m), 1234 (m), 1166 (s), 1204 (m), 1193 (m), 1152 (m), 1101 (w), 1070 (w), 1039 (w), 993 (w), 932 (w), 866 (w), 842 (w), 762 (w), 734 (w), 664 (w) cm^{-1}. HRMS calcd. for $C_7H_6F_6N_2O_2$ + H: 265.04117; found 265.04031.

1-Acetyl-5-hydroxy-3,5-dimethylpyrazoline (1b):[5] A solution of acetohydrazide (55.8 mmol) in ethanol (60 mL) was added to a solution of 2,4-pentadione (**7a**, 55.8 mmol) in ethanol (60 mL). After refluxing the mixture for 5 h the solvent was removed under vacuum. The colorless residue was purified by recrystallization from *n*-hexane; yield 6.0 g (69%, colorless crystals). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 4.78 (br. s, 1 H, OH), 2.64–3.20 (m, 2 H, CH_2), 2.20 (m, 3 H), 1.96 (m, 3 H), 1.78 (m, 3 H) ppm. IR (KBr): $\tilde{\nu}$ = 3412 (m), 2982 (w), 2934 (w), 1648 (s), 1632 (s), 1421 (s), 1377 (s), 1320 (m), 1221 (m), 1117 (m), 964 (m), 940 (w), 866 (w), 742 (w), 638 (w), 560 (w) cm^{-1}. HRMS calcd. for $C_7H_{12}N_2O_2$ + H: 157.09715; found 157.09666.

1-Benzoyl-5-hydroxy-3,5-bis(trifluoromethyl)pyrazoline (1c): A solution of benzohydrazide (55.8 mmol) in ethanol (60 mL) was added to a solution of 1,1,1,5,5,5-hexafluoropeta-2,4-dione (**7b**, 55.8 mmol) in ethanol (60 mL). After refluxing the mixture for 5 h the solvent was removed under vacuum. The colorless residue was purified by recrystallization from ethanol/*n*-hexane (9:1); yield 15.9 g (87%, colorless crystals). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 7.84–7.92 (m, 2 H, Ar), 7.40–7.65 (m, 3 H, Ar), 6.40 (br. s, 1 H, OH), 3.00–3.66 (m, 2 H, CH_2) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 171.6, 144.1, 143.7, 133.3, 131.6, 130.5, 128.3, 94.2, 93.8, 41.4 (CH_2) ppm. ^{19}F NMR (50 MHz, $CDCl_3$, 25 °C): δ = –67.4, –80.5 ppm. IR (KBr): $\tilde{\nu}$ = 3390 (m), 3324 (m), 1680 (s), 1637 (m), 1451 (m), 1434 (m), 1333 (m), 1305 (m), 1275 (s), 1176 (s), 1152 (s), 1078 (m), 1028 (w), 1009 (m), 1009 (m), 905 (w), 792 (w), 757 (w), 715 (w), 672 (w), 631 (w) cm^{-1}. HRMS calcd. for $C_{12}H_8F_6N_2O_2$ + H: 327.05627; found 327.05569.

8a: A solution of dimethylzinc (4.6 mmol, 1.2 M in toluene) was added to a solution of **1a** (4.6 mmol) in toluene (10 mL) at –78 °C. The solution was warmed to room temperature overnight. After removing all volatiles under vacuum a colorless solid was obtained. The residue was crystallized either from *n*-hexane or toluene. Crystals suitable for X-ray diffraction analysis were obtained from a concentrated C_6D_6 solution at room temperature; yield 0.87 g (55%, first harvest, colorless crystals). ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ = 2.80 (m, 2 H, CH_2), 1.73 [s, 3 H, C(=O)CH_3], –0.38 (s, 3 H, ZnCH_3) ppm. ^{13}C NMR (50 MHz, C_6D_6, 25 °C): δ = 177.4, 148.4 (m), 120.6 (m), 98.4 (m), 43.1, 22.5, –16.7 (ZnCH$_3$) ppm. ^{19}F NMR (50 MHz, C_6D_6, 25 °C): δ = –68.4, –82.9 ppm. IR (KBr): $\tilde{\nu}$ = 3384 (m), 2962 (w), 2994 (w), 1698 (s), 1645 (s), 1459 (m), 1378 (m), 1275 (m), 1198 (s), 1027 (m), 996 (m), 876 (m), 876 (m), 760

(m), 734 (w), 658 (m), 581 (m), 501 (m), 474 (w) cm^{-1}. HRMS calcd. for $C_8H_8F_6N_2O_2Zn$ + H: 342.98542; found 342.98542.

8b: A solution of dimethylzinc (12.6 mmol, 1.2 M in toluene) was added to a solution of **1b** (12.6 mmol) in toluene (10 mL) at –78 °C. The solution was warmed to room temperature overnight. After removing all volatiles under vacuum a colorless solid was obtained; yield 0.62 g (21%, first harvest, colorless crystals). ^1H NMR (200 MHz, C_6D_6, 25 °C): δ = 2.87 (br., 1 H, CH_2), 2.77 (br., 1 H, CH_2), 2.07 [s, 3 H, C(=O)CH_3], 1.51 (s, 3 H, CH_3), 1.44 (s, 3 H, CH_3), –0.34 (s, 3 H, ZnCH_3) ppm. ^{13}C NMR (50 MHz, C_6D_6, 25 °C): δ = 171.9, 158.7, 97.1, 54.4, 28.7, 22.4, 16.2, –16.0 (ZnCH_3) ppm. IR (KBr): $\tilde{\nu}$ = 2983 (w), 2939 (w), 2901 (w), 2829 (w), 1635 (w), 1584 (s), 1488 (m), 1418 (m), 1383 (w), 1371 (w), 1321 (m), 1237 (s), 1158 (w), 1111 (m), 1004 (w), 976 (w), 939 (m), 862 (m), 732 (m), 575 (w), 555 (w), 530 (w), 496 (w), 466 (w) cm^{-1}. HRMS calcd. for $C_8H_{14}N_2O_2Zn$ + H: 235.04195; found 235.04234.

8c: A solution of dimethylzinc (6.01 mmol, 1.2 M in toluene) was added to a solution of **1c** (6.01 mmol) in toluene (10 mL) at –78 °C. The solution was warmed to room temperature overnight. After removing all volatiles under vacuum a colorless solid was obtained; yield 1.7 g (72%, colorless crystals from toluene). ^1H NMR (200 MHz, C_6D_6, 25 °C): δ = 7.57–7.69 (m, 2 H, Ar), 6.80–7.00 (m, 3 H, Ar), 2.94–3.15 (m, 2 H, CH_2), –0.29 (s, 3 H, ZnCH_3) ppm. ^{13}C NMR: not detected owing to poor solubility. ^{19}F NMR (50 MHz, C_6D_6, 25 °C): δ = –68.0, –82.1 ppm. IR (KBr): $\tilde{\nu}$ = 2983 (w), 2950 (w), 2917 (w), 2846 (w), 1599 (s), 1572 (s), 1457 (m), 1350 (m), 1279 (m), 1237 (m), 1176 (s), 1075 (m), 1048 (w), 859 (w), 722 (w), 680 (m) cm^{-1}. HRMS calcd. for $C_{13}H_{10}F_6N_2O_2Zn$ + H: 405.00107; found 405.00153.

9a: *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (0.61 mmol) was added dropwise to a solution of **8a** (0.61 mmol) in toluene (10 mL) at room temperature. After stirring for 12 h all volatiles were removed under vacuum to obtain a solid. The colorless residue was purified by recrystallization from *n*-hexane; yield 0.25 g (91%, colorless crystals). ^1H NMR (200 MHz, C_6D_6, 25 °C): δ = 5.79 (s, 1 H,C-*H*), 2.36 (s, 3 H, C-CH_3), 1.74 (s, 12 H, N-CH_3), 1.50 (br., 4 H, CH_2-CH_2) ppm. ^{13}C NMR (50 MHz, C_6D_6, 25 °C): δ = 182.6, 156.0, 157.7, 134.7, 134.4, 129.0, 128.7, 124.6, 123.8, 121.9, 121.0, 84.7, 50.0, 46.1, 18.4 ppm. ^{19}F NMR (50 MHz, C_6D_6, 25 °C): δ = –67.6, –71.7 ppm. IR (KBr): $\tilde{\nu}$ = 2961 (w), 2933 (w), 1619 (m), 1563 (m), 1468 (m), 1404 (w), 1294 (m), 1271 (s), 1181 (s), 1166 (s), 1122 (m), 1105 (m), 1040 (m), 949 (w), 886 (w), 693 (m) cm^{-1}. HRMS calcd. for $C_{13}H_{20}F_6N_4O_2Zn$: 443.08547; found 443.08606.

9b: *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (1.5 mmol) was added dropwise to a solution of **8b** (1.3 mmol) in toluene (10 mL) at 0 °C. After stirring for 12 h at room temperature all volatiles were removed under vacuum to obtain a colorless solid; yield 0.33 g (76%). ^1H NMR (200 MHz, C_6D_6, 25 °C): δ = 4.85 (s, 1 H, C-*H*), 2.47 (s, 3 H), 2.31 (s, 3 H), 2.04 (s, 3 H), 1.96 (s, 12 H, N-CH_3), 1.79 (br., 4 H, CH_2-CH_2) ppm. ^{13}C NMR (50 MHz, C_6D_6, 25 °C): δ = 175.7, 168.4, 161.4, 94.5, 56.5, 46.4, 28.0, 23.0, 20.2 ppm. IR (KBr): $\tilde{\nu}$ = 2967 (w), 2913 (m), 1602 (m), 1533 (s), 1510 (s), 1464 (m), 1418 (s), 1406 (s), 1329 (w), 1273 (m), 1216 (w), 1127 (w), 1029 (m), 1012 (m), 952 (m), 927 (w), 797 (m), 743 (w), 645 (w) cm^{-1}. HRMS calcd. for $C_{13}H_{26}N_4O_2Zn$: 334.14200; found 334.14273.

9c: *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (3.1 mmol) was added dropwise to a solution of **8c** (3.0 mmol) in toluene (10 mL) at 0 °C. After stirring for 12 h at room temperature all volatiles were re-

Table 4. Data collection and refinement parameters for **1a**, **1b**, **1c**, **8a**, **8c** and **9c**.

	1a	**1b**	**1c**	**8a**	**8c**	**9c**
Empirical formula	$C_7H_6F_6N_2O_2$	$C_7H_{12}N_2O_2$	$C_{12}H_8F_6N_2O_2$	$C_{16}H_{16}F_{12}N_4O_4Zn_2$	$C_{26}H_{20}F_{12}N_4O_4Zn_2$	$C_{18}H_{22}F_6N_4O_2Zn_1$
Formula weight [g/mol]	264.14	156.19	326.20	687.07	811.24	505.77
Temperature [K]	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$Pbca$
a [Å]	11.8393(6)	8.7490(6)	13.289(2)	7.2494(2)	13.6470(6)	17.4838(4)
b [Å]	9.0842(4)	9.2277(7)	9.6993(15)	17.0254(4)	9.6084(3)	12.1420(3)
c [Å]	8.5465(9)	21.1708(18)	10.412(2)	9.3704(2)	12.9663(6)	20.2310(6)
α [°]	90	90	90	90	90	90
β [°]	100.378(5)	95.103(7)	100.776(18)	90.787(2)	115.308(6)	90
γ [°]	90	90	90	90	90	90
Volume [Å^3]	1962.05(16)	1702.4(2)	1318.4(4)	1156.42(5)	1537.03(11)	4294.80(19)
Z	8	8	4	2	2	8
$D_{calcd.}$ [g/cm^3]	1.788	1.219	1.643	1.973	1.753	1.564
F(000)	1056	672	656	680	808.0	2064
Crystal size [mm]	0.27 × 0.21 × 0.09	0.42 × 0.40 × 0.09	0.49 × 0.42 × 0.36	0.32 × 0.31 × 0.28	0.35 × 0.23 × 0.14	0.57 × 0.25 × 0.23
θ range [°]	2.94 to 25.00	3.56 to 25.00	3.46 to 25.00	3.53 to 25.00	3.30 to 25.00	3.36 to 25.00
Index ranges	$-14 \le h \le 14$	$-10 \le h \le 10$	$-15 \le h \le 15$	$-8 \le h \le 4$	$-16 \le h \le 16$	$-19 \le h \le 20$
	$-10 \le k \le 10$	$-10 \le k \le 10$	$-11 \le k \le 10$	$-20 \le k \le 19$	$-7 \le k \le 11$	$-14 \le k \le 6$
	$-22 \le l \le 20$	$-9 \le l \le 25$	$-9 \le l \le 12$	$-11 \le l \le 10$	$-15 \le l \le 15$	$-14 \le l \le 24$
Refl. collected	9805	5619	4899	4354	5552	14049
Independent refl.	3461	2993	2317	1989	2698	3779
[R(int)]	[0.0771]	[0.0714]	[0.0279]	[0.0190]	[0.0278]	[0.0355]
Completeness to θ = 25.00° [%]	99.8	99.7	99.8	97.8	99.8	99.8
Rel. transm. factors	0.950 and 0.982	0.963 and 0.992	0.942 and 0.922	0.539 and 0.577	0.584 and 0.799	0.544 and 0.767
Parameters	311	207	200	174	218	284
GOF	0.858	0.834	0.970	1.010	0.925	0.925
R_1 [$I > 2\sigma(I)$][a]	0.0515	0.0592	0.0429	0.0255	0.0299	0.0290
wR_2 [$I > 2\sigma(I)$][b]	0.0572	0.0683	0.0978	0.0587	0.0587	0.0545
R_1 (all data)[a]	0.0572	0.1664	0.0681	0.0322	0.0429	0.0492
wR_2 (all data)[b]	0.0691	0.0858	0.1061	0.0601	0.0606	0.0577

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma F_o$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

moved under vacuum. The obtained orange solid was crystallized from *n*-hexane/toluene (5:1) to give colorless crystals. The crystals were filtered off and dried under vacuum. Crystals suitable for X-ray diffraction analysis were obtained from a concentrated C_6D_6 solution at room temperature overnight; yield 1.3 g (84%, colorless crystals). ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ = 8.30–8.38 (m, 2 H, C_6H_5), 7.07–7.25 (m, 3 H, C_6H_5), 5.79 (s, 1 H, =C*H*), 1.82 [s, 12 H, N(CH_3)$_2$], 1.63 (br., 4 H, CH_2-CH_2) ppm. ^{13}C NMR (50 MHz, C_6D_6, 25 °C): δ = 177.7, 156.9, 156.4, 137.0, 136.4, 134.1, 131.7, 131.0, 85.0, 56.5, 46.5 ppm. ^{19}F NMR (50 MHz, C_6D_6, 25 °C): δ = –67.2, –71.6 ppm. IR (KBr): $\tilde{\nu}$ = 2928 (w), 1622 (s), 1468 (m), 1400 (m), 1304 (m), 1275 (m), 1192 (s), 1124 (s), 1024 (m), 952 (w), 846 (m), 804 (w), 786 (w), 731 (w), 689 (w) cm^{-1}. HRMS calcd. for $C_{18}H_{22}F_6N_4O_2Zn$: 505.10112; found 505.10239.

Single-Crystal X-ray Structure Determination: Crystals were mounted on a glass capillary in perfluorinated oil and measured in a cold N_2 flow. The data were collected using an Oxford Diffraction Xcalibur S Sapphire at 150(2) K (Mo-K_α radiation, λ = 0.71073 Å). The structures were solved by direct methods and refined on F^2 with the SHELX-97 software package.[14] The positions of the hydrogen atoms were calculated and considered isotropically according to a riding model (Table 4).

CCDC-816673 (for **1a**), -816674 (for **1b**), -816675 (for **1c**), -816676 (for **8a**), -816678 (for **8c**) and -816677 (for **9c**) 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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