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A new anilido-imine compound containing *o*-OMe-anilinyll derived from an unexpected adduct: Synthesis, crystal structure and its coordination capability

Qing Su^a, Pei Li^a, Mina He^a, Qiaolin Wu^{a,*}, Ling Ye^b, Ying Mu^{a,b,*}, Yudan Ma^c^a School of Chemistry, Jilin University, 2699 Qianjin Street, Chang Chun 130012, People's Republic of China^b State Key Laboratory of Supramolecular Structure and Materials, Jilin University, 2699 Qianjin Street, Chang Chun 130012, People's Republic of China^c Sports Science Research Institute of Jilin Province, 2476 Ziyou Road, Changchun 130022, People's Republic of China

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ABSTRACT

A new compound, *ortho*-C₆H₄F[CH(NHC₆H₄OMe-2)]₂, **1**, was obtained with *ortho*-flurobenzaldehyde and 2-methoxyaniline as the starting materials. Compound **1** was readily converted into *ortho*-C₆H₄(2-OMeC₆H₄)(CH=NC₆H₄OMe-2) **2** after treatment with 1 equiv of *n*-BuLi. Treatment of compound **2** with 1.5 equiv of ZnEt₂ afforded the trinuclear zinc complex **3** by alkyl elimination and alkylation of the imino group of the ligand. The molecular structures of two new organic compounds and of the trinuclear zinc complex were determined by single-crystal X-ray diffraction. The dianionic ONNO tetradentate ligands derived from compound **2** coordinate to zinc ions in four to five coordination modes, forming distorted tetrahedral and trigonal-bipyramidal geometry around three metal centers.

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1. Introduction

Various types of metal complexes, such as Y(III) [1], Zn(II) [2], Al(III) [3], B(III) [4], Ni(II) [5], Cu(II) [6–8] with chelating anilido-imine (Fig. 1, I) ligands have received extensive attention in recent years due to their applications in coordination chemistry and catalysis. The anilido-imine compounds have similar frameworks and combine the steric and electronic features of the β -diketiminato (Fig. 1, II) and salicylaldiminato (Fig. 1, III) ligand frameworks extensively researched in bioinorganic and transition metal chemistry [9,10]. The general method for the synthesis of anilido-imine compounds involved the condensation of the *ortho*-flurobenzaldehyde with 1 equiv of amine to form a Schiff base and the subsequently nucleophilic substitution of the Schiff base by aromatic

amide lithium (Scheme 1). Previously, we have reported the luminescent properties and coordination chemistry of Zn(II) complexes supported by anilido-imine and salicylaldiminato ligands [2c,11]. As part of our continuing study, we designed a new multidentate anilido-imine compound (Fig. 1, 2) containing *o*-OMe-anilinyll, which has two N and two O donor atoms and could be used to synthesize polynuclear metal complexes with Zn(II) ions. Thus we tried to synthesize *ortho*-C₆H₄F(CH=NC₆H₄OMe-2) with *ortho*-flurobenzaldehyde and 2-methoxyaniline as the starting materials according to the literature [1]. However, a new compound **1** with formula *ortho*-C₆H₄F[CH(NHC₆H₄OMe-2)]₂ was always obtained.

As we know, the reaction of 1,2-diamine with substituted aldehydes produces the corresponding imidazolidine, which are the intermediates for the synthesis of substituted dihydroimidazole [12]. To the best of our knowledge, there are few reports on the reaction of amine with substituted aldehydes to form the phenylmethane-diamine. Furthermore, compound **1** was readily converted

* Corresponding authors.

E-mail address: wuql@jlu.edu.cn (Q. Wu).

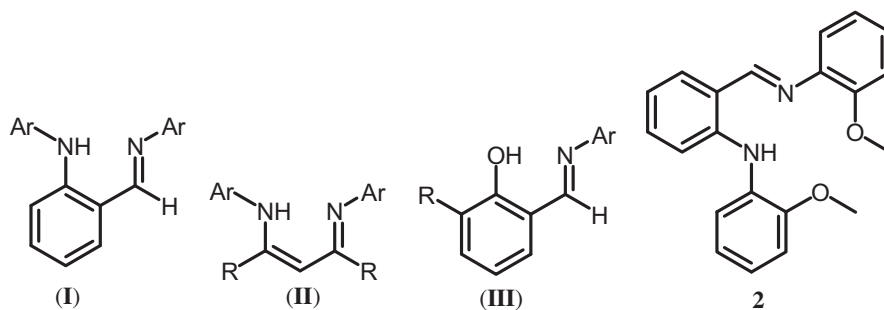
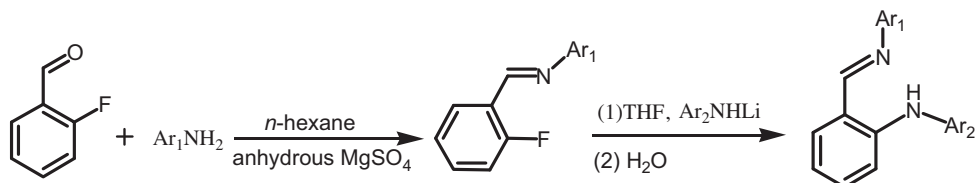


Fig. 1. Molecular structure of anilido-imine (I), β -diketiminato (II), salicylaldiminato (III) and object compound (2).



Scheme 1. Synthetic routes for anilido-imine compounds.

into the anilido-imine compound by treatment with *n*-BuLi. The new anilido-imine compound could be used as a potentially multidentate ligand for preparing polynuclear metal complexes. Herein, we wish to report the synthesis and characterization of a new multidentate anilido-imine compound containing *o*-OMe-anilanyl and the corresponding zinc complex, as well as their specific structural features.

2. Experimental

2.1. General comments

All organometallic reactions were performed using standard Schlenk techniques under a high-purity argon atmosphere or glovebox techniques. *n*-Hexane, THF, and toluene were dried by refluxing over sodium and benzophenone and distilled under argon prior to use. *n*-BuLi was purchased from Aldrich and used as received. ^1H and ^{13}C NMR spectra were measured using a Varian Mercury-300 or Bruker Avance 500 NMR spectrometer. The elemental analyses were performed on an Elementar Vario EL cube analyzer. IR spectra were recorded on an IRAffinity-1 spectrometer using KBr pellets. All melting points were determined by an X-5 micro-melting point apparatus and are uncorrected.

2.2. Synthesis of *ortho*- $\text{C}_6\text{H}_4\text{F}[\text{CH}(\text{NHC}_6\text{H}_4\text{OMe-2})_2]$ (1)

A mixture of *ortho*-fluorobenzaldehyde (5.00 mL, 47.5 mmol) and 2-methoxyaniline (10.70 mL, 95.0 mmol) in *n*-hexane (50 mL) was stirred at room temperature overnight. A lot of white solid is formed. The mixture was filtered and washed with *n*-hexane (4 mL \times 3) under reduced pressure. The white solid product was dried in vacuo. Yield: 15.90 g, 95.0%. mp 76–78 °C. Anal. calcd for $\text{C}_{21}\text{H}_{21}\text{FN}_2\text{O}_2$ (352.4): C 71.57, H 6.01, N 7.95. Found: C

71.58, H 5.91, N 7.95%. ^1H NMR (300 MHz, $\text{DMSO-}d_6$, 298 K): δ = 3.74 (s, 3H, OCH₃), 3.80 (s, 2 \times 3H, OCH₃), 4.67 (br, 2H, ArNH), 6.48–6.54 (m, 1H), 6.60–6.69 (m, 2H), 6.77 (dd, 1H, J = 1.2 Hz, 9.0 Hz), 6.97 (dt, 1H, J = 1.2 Hz, 9 Hz), 7.08 (dd, 2H, J = 1.5 Hz, 8.1 Hz), 7.19–7.25 (m, 1H), 7.32–7.39 (m, 2H), 7.57–7.64 (m, 1H), 8.08 (dt, 1H, J = 1.8 Hz, 9 Hz), 8.71 (s, 1H) ppm. ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$, 298 K): δ = 55.1 (OCH₃), 55.5 (OCH₃), 110.5, 112.1, 113.8, 116.1, 120.5, 120.8, 120.9, 124.8, 124.9, 127.0, 127.7, 127.8, 133.4, 133.6, 137.6, 141.0, 146.3, 151.8, 153.8 ppm. IR (KBr, cm^{-1}): ν 3425 (N–H), 3364 (N–H), 3065, 3042, 3016, 2962, 2936, 2902, 2834, 1844, 1802, 1598, 1507, 1487, 1458, 1419, 1361, 1339, 1320, 1251, 1243, 1224, 1176, 1151, 1136, 1123, 1104, 1088, 1061, 1051, 1019, 949, 897, 855, 832, 810, 779, 763, 732, 647, 591, 521, 461.

2.3. Synthesis of *ortho*- $\text{C}_6\text{H}_4(2\text{-OMeC}_6\text{H}_4)(\text{CH}=\text{NC}_6\text{H}_4\text{OMe-2})$ (2)

A solution of *n*-BuLi (8.9 mL, 1.60 mol/L, 14.2 mmol) in *n*-hexane was added to a solution of *ortho*- $\text{C}_6\text{H}_4\text{F}[\text{CH}(\text{NHC}_6\text{H}_4\text{OMe-2})_2]$ (5.00 g, 14.2 mmol) in THF (40 mL) at -78°C . The mixture was allowed to warm to room temperature and stirred for four days. The reaction was quenched with H_2O (20 mL). The water phase was extracted with ethyl ether (20 mL \times 2). The combined organic phase was dried over anhydrous MgSO_4 and evaporated to dryness to give the crude product as a brown-red oil, which was further purified by column chromatography on silica gel with ethyl acetate/petroleum ether (1:2 in volume) as the eluent to give the pure product as yellowish crystals (4.10 g, 87.0%). mp 78–80 °C. Anal. calcd. for $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_2$ (332.4): C 75.88, H 6.06, N 8.43. Found: C 75.84, H 6.04, N 7.97%. ^1H NMR (500 MHz, CDCl_3 , 298 K): δ = 3.90 (s, 2 \times 3H, OCH₃), 6.83 (t, 1H, J = 7.0 Hz), 7.03 (m, 5H), 7.14 (dd, 1H, J = 1.5, 8.0 Hz), 7.21 (dt, 1H, J = 1.5, 7.0 Hz), 7.29 (m, 1H) 7.38 (d, 1H, J = 12.5 Hz), 7.45

(d, 1H, $J = 7.5$ Hz), 7.57 (d, 1H, $J = 3.5$ Hz), 8.69 (s, 1H, CH=NAr), 11.25 (s, 1H, NH) ppm. ^{13}C NMR (125 MHz, CDCl_3 , 298 K): $\delta = 55.8$ (OCH₃), 56.1 (OCH₃), 113.4, 117.0, 119.6, 120.6, 120.9, 121.1, 121.2, 123.2, 126.4, 130.8, 131.6, 134.8, 140.9, 146.0, 151.9, 152.5, 163.4 (CH=N) ppm. IR (KBr, cm^{-1}): ν 3462, 3006, 2956, 1844, 1811, 1771, 1620, 1589, 1571, 1524, 1495, 1456, 1383, 1338, 1249, 1173, 1159, 1114, 1047, 1028, 972, 913, 839, 752, 743.

2.4. Synthesis of trinuclear zinc complex 3

A solution of *ortho*-C₆H₄(2-MeO-C₆H₄NH)(CH=NC₆H₄OMe-2) (0.25 g, 0.8 mmol) in toluene (10 mL) was slowly added to a solution of ZnEt₂ (1.20 mmol) in toluene (10 mL) at room temperature under stirring. The mixture was stirred at room temperature for 1 h and at 80 °C for an additional 4 h. The solvent was removed in vacuo, and the obtained orange-red residue was recrystallized from *n*-hexane/toluene ($v/v = 5:1$, 5 mL) to give an orange-red solid (0.17 g, 45%). ^1H NMR (300 MHz, C₆D₆, 298 K): $\delta = 0.54$ (q, $J = 7.5$ Hz, 2H, ZnCH₂CH₃), 0.84 (t, $J = 7.5$ Hz, 3H, CHCH₂CH₃), 1.17 (t, $J = 7.5$ Hz, 3H, ZnCH₂CH₃), 1.74–1.86 (m, 2H, CHCH₂CH₃), 3.30 (s, 6H, OCH₃), 3.40 (s, 6H, OCH₃), 4.72 (d, $J = 6.0$ Hz, 2H, CHCH₂CH₃), 5.86 (d, $J = 6.0$ Hz, 1H, Ph-H), 6.10 (d, $J = 6.0$ Hz, 1H, Ph-H), 6.26 (d, $J = 6.0$ Hz, 1H, Ph-H), 6.38–6.44 (m, 2H, Ph-H), 6.51 (t, $J = 6.0$ Hz, 1H, Ph-H), 6.60–6.68 (m, 4H, Ph-H), 6.71–6.75 (m, 2H, Ph-H), 6.82–6.87 (m, 4H, Ph-H), 6.90–6.95 (m, 2H, Ph-H), 7.06–7.11 (m, 2H, Ph-H), 7.29–7.38 (m, 2H, Ph-H), 7.45–7.55 (m, 2H, Ph-H) ppm. IR (KBr, cm^{-1}): ν 2934 (w), 2842 (w), 2360 (w), 1594 (m), 1490 (s), 1450 (m), 1231 (s), 1171 (m), 1115 (m), 1015 (m), 890 (w), 732 (s), 502 (w), 441 (w).

2.5. X-ray structure determinations of 1–3

The single-crystal X-ray diffraction data for **1–3** were collected on a Rigaku R-Axis RAPID IP diffractometer equipped with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å), operating at 293 ± 2 K. The structures were solved by direct method [13] and refined by full-matrix least squares based on F^2 using the SHELXTL 5.1 software package

[14]. All non-hydrogen atoms were refined anisotropically. Unless otherwise noted, hydrogen atoms were included in idealized position and were allowed to ride.

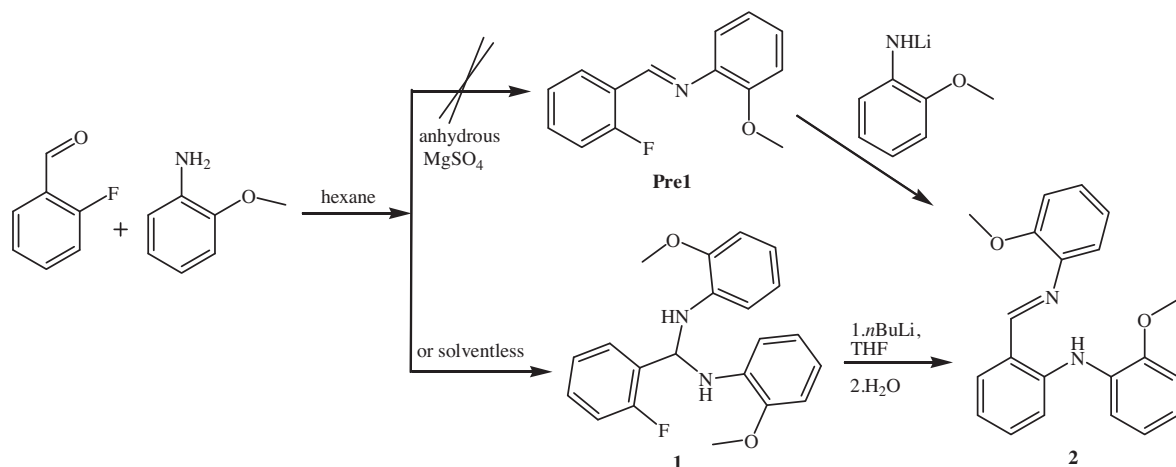
3. Results and discussion

3.1. Synthesis of compounds 1 and 2

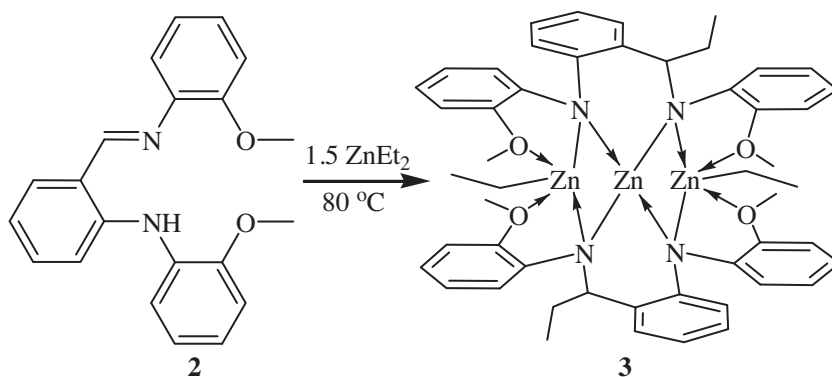
A lot of known Schiff compounds *ortho*-C₆H₄F(CH=NAr') (Ar' = 2,6-*i*Pr₂C₆H₃, 2,6-Me₂C₆H₃, 2,6-Et₂C₆H₃, 4-MeC₆H₄, Ph) [1,2,3,5,7,11] have been readily synthesized by condensation reaction of *ortho*-fluorobenzaldehyde with 1 equiv of the relevant amine in *n*-hexane in the presence of anhydrous MgSO₄. However, a new compound, *ortho*-C₆H₄F[CH(NHC₆H₄OMe-2)₂] **1**, was formed by the reaction of *ortho*-fluorobenzaldehyde with 1 equiv of 2-methoxyaniline in similar condition, with trace amounts of *ortho*-C₆H₄F(CH=NC₆H₄OMe-2) (**Pre1**) obtained as a by-product (Scheme 2). The new compound *ortho*-C₆H₄F[CH(NHC₆H₄OMe-2)₂] **1** was readily obtained when the two liquid raw materials were mixed together in *n*-hexane or free of solvent in any ratio. The highest yield was obtained when the mole ratio of the *ortho*-fluorobenzaldehyde to 2-methoxyaniline is 1:2.

Compound **1** is insoluble in water, slightly soluble in *n*-hexane, while soluble in hot *n*-hexane, toluene, and THF. Fortunately, white crystals suitable for X-ray crystal structure determination were obtained in *n*-hexane at room temperature. The detailed crystal structure information will be shown in the crystal description section. Compound **2** was readily synthesized by the reaction of compound **1** with 1 equiv of *n*-BuLi in THF (Scheme 2) and purified by chromatography on silica gel with ethyl acetate/petroleum ether as the eluent to give pure products as yellowish crystals. Compound **2** is soluble in common solvents, such as *n*-hexane, methylene chloride, chloroform, ethyl acetate, toluene, and THF.

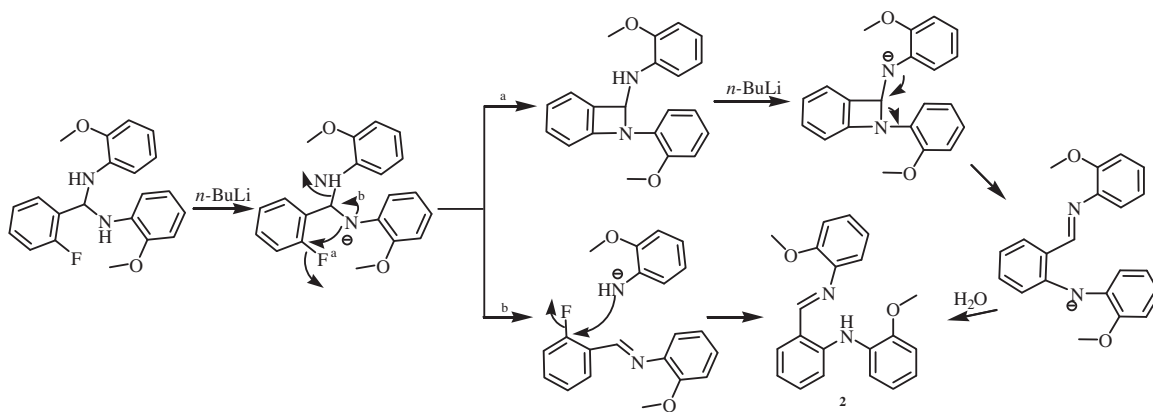
Both compounds **1** and **2** were characterized by ^1H and ^{13}C NMR spectroscopy, IR along with elemental analysis, and satisfactorily analytic results were obtained. Compound **1** was found to decompose gradually in



Scheme 2. Synthetic routes for compounds **1** and **2**.



Scheme 3. Synthetic route for complex 3.



Scheme 4. The probable mechanism for the formation of compound 2.

chloroform due to its sensitivity to acids or acidic solvents. The ^1H NMR and ^{13}C NMR spectra of compound **1** in a deuterated DMSO solution were obtained. The ^1H NMR spectrum of **1** exhibits a broad resonance at $\delta = 4.67$ ppm for the NH proton. The methylene CH proton of compound **1** exhibits a resonance at 8.71 ppm and the corresponding methylene CH carbon exhibits a resonance at 153.8 ppm. The ^1H NMR spectrum of **2** exhibits a resonance at $\delta = 8.69$ ppm for the imino CH proton, while the corresponding ^{13}C NMR resonance is at $\delta = 163.4$ ppm. Compared with the ^1H NMR spectrum of **1**, the NH proton resonance at 4.67 ppm disappeared and a characteristic NH proton resonance for anilido-imine compound **2** at 11.25 ppm appeared, which were comparable to other reported compounds of this type 10.53–11.64 ppm for *ortho*- $\text{C}_6\text{H}_4\{\text{NH}(\text{C}_6\text{H}_3\text{Ar})\}(\text{CH}=\text{NAr}')$ [2c,3a,3b,15].

The IR data is consistent with the presented structures. The middle strong band at *ca.* 1123 cm^{-1} associated with the C–F stretching vibration is present in the IR spectrum of compound **1**. The characteristic strong band at *ca.* 1620 cm^{-1} associated with the imine C=N stretching vibration is present in the IR spectrum of compound **2**.

3.2. Synthesis of trinuclear zinc complex 3

The reaction of compound **2** with 1.5 equiv of ZnEt_2 at $80\text{ }^\circ\text{C}$ caused the elimination of ethylene and alkylation of

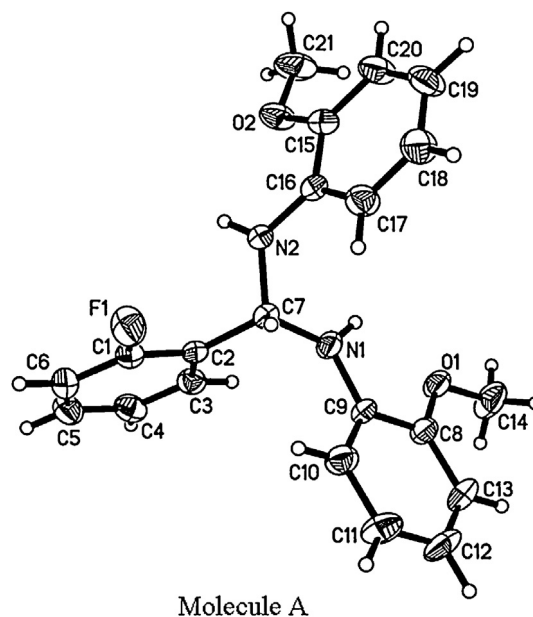


Fig. 2. Molecular structure of compound **1** (the other molecule has been omitted for clarity). The thermal ellipsoids are drawn at 30% probability levels.

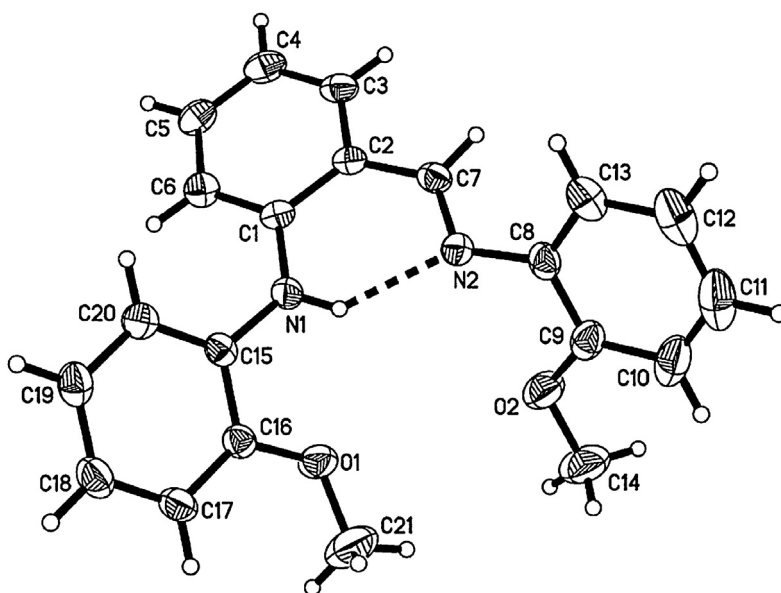


Fig. 3. Molecular structure of compound **2** (the thermal ellipsoids are drawn at 30% probability levels).

the imino group of the ligand, and further yields the trinuclear zinc complex **3** (Scheme 3). ^1H NMR analysis of complex **3** revealed a characteristic set of peaks for the dianionic tetradentate ligand and the coordinated ethyl group. The N–H proton signal of the free ligands disappeared, and the new Zn–CH₂CH₃ proton signals appeared at a higher field (0.54–0.84 ppm), which is indicative of the formation of a Zn–N bond in the new complex. The absence of the signal for the imino proton suggested the alkylation of the imino group of the ligand, which was also confirmed by the formation of a CH(CH₂CH₃)N group exhibiting discrete multiple resonances, assigned to the methylene protons. The OMe protons showed a high field shift at 3.30 and 3.40 ppm compared to those at 3.90 ppm for the free ligand, suggesting that the OMe moiety coordinated to the zinc ion in a η^1 -fashion. The IR spectrum of complex **3** showed a strong band at 1231 cm⁻¹ attributed to the C–N stretching vibration and the disappearance of the C=N stretching vibration bands at 1620 cm⁻¹, which also indicated the alkylation of the imino group of the ligand. Moreover, the Zn–N stretching vibration is observed at 441 and 502 cm⁻¹.

3.3. The probable mechanisms for the formation of anilido-imine **2**

Two probable mechanisms involving the transformation of the compound **1** to compound **2** in the presence of *n*-BuLi have been proposed, as shown in Scheme 4. When treated the compound **1** with 1 equiv of *n*-BuLi, one of the secondary amines was deprotonated. Then, the nucleophilic nitrogen anion could attack the C–F bond in the central aromatic ring (Scheme 4 route a) or the C–N bond in the same carbon atom (Scheme 4 route b). According to the route a, the C–F bond cleavage occurs and a new C–N bond forms, resulting in a new four-membered nitrogen-containing heterocycle. Then, the other secondary amine

was further deprotonated by 1 equiv of *n*-BuLi. The formed nitrogen anion could attack the C–N bond in the four-membered ring to cause a ring-opening reaction of the four-membered nitrogen-containing heterocycle, resulting in the formation of a C=N bond and an anilido anion. After hydrolysis with 1 equiv of H₂O, *ortho*-C₆H₄(2-OMeC₆H₄)(CH=NC₆H₄OMe-2) is produced. According to route b, the Schiff base *ortho*-C₆H₄F(CH=NC₆H₄OMe-2) and lithium 2-methoxy-phenylamine are produced in the nucleophilic reaction. The C–F bond in *ortho*-C₆H₄F(CH=NC₆H₄OMe-2) should be further substituted by lithium 2-methoxyphenylamine in a nucleophile way to

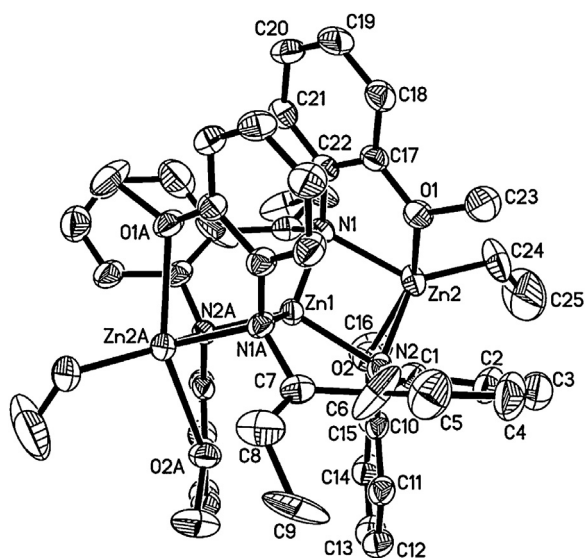


Fig. 4. Molecular structure of the trinuclear zinc complex **3** (all the hydrogen atoms have been omitted for clarity. The thermal ellipsoids are drawn at 30% probability levels).

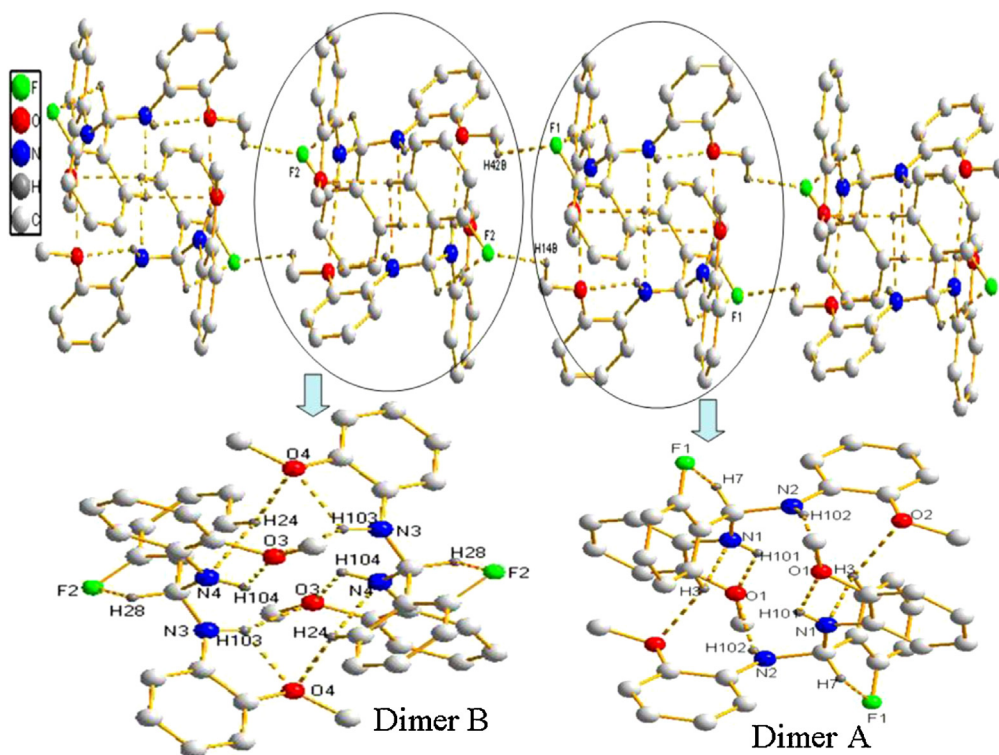


Fig. 5. (Color online.) Packing of compound **1** (hydrogen bonds are indicated by dashed lines; the hydrogen atoms not involved in hydrogen bonds are omitted for clarity).

Table 1
Crystal data and structural refinements details for **1–3**.

	1	2	3
Formula	C ₂₁ H ₂₁ FN ₂ O ₂	C ₂₁ H ₂₀ N ₂ O ₂	C ₅₀ H ₅₈ N ₄ O ₄ Zn ₃
Fw	352.4	332.39	975.11
Temperature/K	293(2)	293(2)	293(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2(1)	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	12.268(3)	11.736(2)	17.954(4)
<i>b</i> /Å	12.391(3)	7.3385(15)	13.364(3)
<i>c</i> /Å	13.236(3)	11.975(2)	19.999(4)
α /°	75.84(3)	90	90
β /°	67.39(3)	119.23(3)	108.54(3)
γ /°	76.59(3)	90	90
Volume (Å ³)	1779.5(6)	900.1(3)	4549.3(16)
Z	4 ^a	2	4
<i>D</i> _{calcd} (Mg.m ⁻³)	1.315	1.226	1.424
<i>F</i> (000)	744	352	2032
θ range for data collection	3.23–27.48	3.39–27.48	3.05–27.47
Limiting indices	$-15 \leq h \leq 15$, $-16 \leq k \leq 16$, $-17 \leq l \leq 17$	$-14 \leq h \leq 15$, $-9 \leq k \leq 9$, $-15 \leq l \leq 15$	$-21 \leq h \leq 23$, $-17 \leq k \leq 16$, $-25 \leq l \leq 25$
Data/restraints/parameters	7949/0/482	3940/1/232	5160/18/281
Goodness-of-fit on <i>F</i> ²	1.046	1.040	1.041
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ ^b = 0.1258, <i>wR</i> ₂ ^c = 0.3184	<i>R</i> ₁ ^b = 0.0401, <i>wR</i> ₂ ^c = 0.0819	<i>R</i> ₁ ^b = 0.0841, <i>wR</i> ₂ ^c = 0.2031
<i>R</i> indices (all data)	<i>R</i> ₁ ^b = 0.2130, <i>wR</i> ₂ ^c = 0.3737	<i>R</i> ₁ ^b = 0.0634, <i>wR</i> ₂ ^c = 0.0888	<i>R</i> ₁ ^b = 0.1606, <i>wR</i> ₂ ^c = 0.2421
Largest diff. peak and hole/e-Å ⁻³	0.672/–0.339	0.101/–0.107	1.398/–0.520

^a There are two crystallographically independent molecules in the asymmetric unit.

^b $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^c $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$.

produce *ortho*-C₆H₄(2-OMeC₆H₄)(CH=NC₆H₄OMe-2). In route a, 2 equiv of *n*-BuLi are needed, while 1 equiv of *n*-BuLi is needed in route b. Compound **1** was treated with 1 equiv of *n*-BuLi and 2 equiv of *n*-BuLi, respectively. The results indicated that only 1 equiv of *n*-BuLi was needed. So, route b is more probable, as indicated by the total amount of *n*-BuLi during the reaction (Scheme 4).

3.4. Crystal structures of 1–3

The molecular structures of **1–3** were determined by X-ray crystallographic analysis. Crystals of compound **1** suitable for X-ray crystal structure determination were grown from *n*-hexane at room temperature. Crystals of compound **2** suitable for X-ray crystal structure determination were grown from ethyl acetate/petroleum ether at room temperature. Crystals of trinuclear zinc complex **3** suitable for X-ray crystal structure determination were

grown from toluene/*n*-hexane at room temperature. The ORTEP drawings of molecular structures of **1–3** are shown in Figs. 2–4, respectively. The crystallographic and refinement data for **1–3** are summarized in Table 1. Hydrogen bond geometries for **1** and **2** are given in Table 2. Selected bond lengths and angles for **3** are given in Table 3.

X-ray analysis reveals that the unit cell of **1** contains two independent molecules, one (molecule **A**) of which is shown in Fig. 2. The dihedral angles among phenyl rings are 94.4°, 102.7° and 71.2° (102.8°, 99.4° and 88.2° in molecule **B**), respectively. In molecule **A**, there exist an intramolecular C–H...F interaction with an S(5) motif, a ¹⁶C–H...N interaction with an S(5) motif and a N–H...O interaction with an S(5) motif. Two adjacent molecules **A** form a dimer **A** through intermolecular N–H...O and C–H...O interactions. There are similar interactions in molecules **B**. Dimer **A** and dimer **B** were further linked through the intermolecular C–H...F interactions to form a 3-D network (Fig. 5).

Table 2
Hydrogen bond geometries for **1** and **2**.

Structure	D–H...A	<i>d</i> (D–H)(Å)	<i>d</i> (H...A)(Å)	<i>d</i> (D...A)(Å)	<(DHA) (deg)
1^a	N(2)–H(102)...O(1)#1	0.86	2.60	3.382(6)	151.2
	N(1)–H(101)...O(1)	0.83(6)	2.16(6)	2.620(5)	115(5)
	N(2)–H(102)...O(2)	0.86	2.36	2.631(6)	98.9
	N(3)–H(103)...O(4)	0.93(6)	2.13(6)	2.645(6)	114(5)
	N(3)–H(103)...O(3)#2	0.93(6)	2.43(7)	3.281(6)	152(5)
	N(4)–H(104)...O(3)	0.86	2.24	2.611(5)	106.3
	C(3)–H(3)...N(1)	0.93	2.55	2.867(7)	100.3
	C(24)–H(24)...N(4)	0.93	2.52	2.857(7)	101.4
	C(3)–H(3)...O(2)#1	0.93	2.70	3.438(7)	136.5
	C(42)–H(42B)...F(1)#3	0.96	2.72	3.270(7)	116.8
	C(7)–H(7)...F(1)	0.98	2.50	2.817(5)	98.3
	C(14)–H(14B)...F(2)#4	0.96	2.81	3.394(7)	120.4
	C(28)–H(28)...F(2)	0.98	2.53	2.811(6)	96.4
	C(24)–H(24)...O(4)#2	0.93	2.64	3.412(6)	140.9
	2^b	C(14)–H(14C)...O(2)#1	0.96	2.61	3.500(3)
N(1)–H(1)...N(2)		0.85(2)	2.018(18)	2.698(2)	136.9(17)

^a #1 – *x*, –*y*, –*z*+1; #2 – *x*+1, –*y*+1, –*z*+2; #3 *x*, *y*+1, *z*+1; #4 *x*–1, *y*, *z*.

^b #1 – *x*, *y*–1/2, –*z*+1.

Table 3
Selected bond lengths [Å] and angles [°] for **3**.

Complex 3^a			
Zn(1)–N(1)	2.009(5)	N(1)–Zn(1)–Zn(2)#1	130.85(15)
Zn(1)–N(2)	2.040(5)	N(2)#1–Zn(1)–Zn(2)#1	49.83(16)
Zn(2)–N(1)	2.118(5)	N(2)–Zn(1)–Zn(2)#1	129.75(16)
Zn(2)–N(2)	2.130(6)	C(24)–Zn(2)–N(1)	134.1(4)
Zn(2)–O(1)	2.387(5)	C(24)–Zn(2)–N(2)	132.7(4)
Zn(2)–O(2)	2.441(5)	N(1)–Zn(2)–N(2)	93.2(2)
Zn(2)–C(24)	1.980(8)	C(24)–Zn(2)–O(1)	103.0(3)
C(1)–N(2)	1.459(9)	N(1)–Zn(2)–O(1)	71.80(19)
C(7)–N(1)#1	1.486(9)	N(2)–Zn(2)–O(1)	90.68(19)
Zn(1)–Zn(2)#1	2.7684(10)	C(24)–Zn(2)–O(2)	101.7(3)
N(1)#1–Zn(1)–N(1)	129.8(3)	N(1)–Zn(2)–O(2)	92.33(18)
N(1)#1–Zn(1)–N(2)#1	99.4(2)	N(2)–Zn(2)–O(2)	70.8(2)
N(1)–Zn(1)–N(2)#1	102.2(2)	O(1)–Zn(2)–O(2)	155.21(17)
N(1)#1–Zn(1)–N(2)	102.2(2)	C(7)#1–N(1)–Zn(1)	108.8(4)
N(1)–Zn(1)–N(2)	99.4(2)	C(7)#1–N(1)–Zn(2)	113.5(4)
N(2)#1–Zn(1)–N(2)	127.6(3)	Zn(1)–N(1)–Zn(2)	84.2(2)
N(1)#1–Zn(1)–Zn(2)#1	49.56(15)	Zn(1)–N(2)–Zn(2)	83.2(2)
C(1)–N(2)–Zn(1)	111.2(4)	C(22)–N(1)–Zn(1)	117.1(4)
C(10)–N(2)–Zn(1)	117.6(4)	C(22)–N(1)–Zn(2)	114.2(4)
C(1)–N(2)–Zn(2)	111.5(4)	C(10)–N(2)–Zn(2)	116.1(4)

^a Symmetry transformations used to generate equivalent atoms: #1 – *x*, *y*, –*z*+1/2.

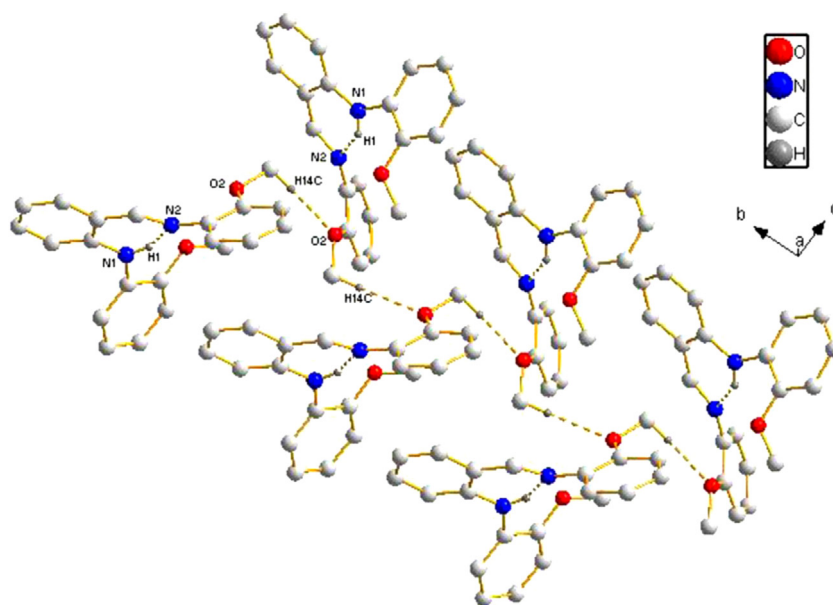


Fig. 6. (Color online.) Packing of compound **2** (hydrogen bonds are indicated by dashed lines; the hydrogen atoms not involved in hydrogen bonds are omitted for clarity).

In molecule **2**, the bond lengths and angles are within normal range. The C=N bond length [1.272(2) Å] is comparable to those found in similar anilido-imine compounds, such as *ortho*-C₆H₄{7-NH(2,4-Me₂)C₉H₄N}(CH=NC₆H₃Me₂-2,6) [1.271(2) Å] [2c], *ortho*-C₆H₄{7-NH(2,4-Me₂)C₉H₄N}(CH=NC₆H₃Et₂-2,6) [1.267(4), 1.275(4) Å] [2c], and *ortho*-C₆H₄(4-OMeC₆H₄)(CH=NC₆H₃Et₂-2,6) [1.2730(15) Å] [15]. The dihedral angles between the central benzene ring (C1/C2/C3/C4/C5/C6) and the two MeO-substituted benzene rings of the anilido-imine compound are 57.8° (C8/C9/C10/C11/C12/C13), and 132.8° (C15/C16/C17/C18/C19/C20), respectively. The dihedral angle between the two MeO-substituted benzene rings (ring C8/C9/C10/C11/C12/C13 and ring C15/C16/C17/C18/C19/C20) is 109.5°. An intramolecular N–H...N hydrogen bond forms a six-membered ring, generating an S(6) motif [16]. In the packing of the crystal, the adjacent molecules were linked through intermolecular C–H...O interactions [3.500(3) Å, 154.2°, -x, y - 1/2, -z + 1] arising from the interactions between the oxygen atom of the methoxyl in the phenyl ring bonding to the anilido nitrogen atom and the hydrogen atom of the methoxyl in the phenyl ring bonding to the imino nitrogen atom to form a 1-D S-shaped chain (Fig. 6). There are no interactions between each adjacent chain.

Trinuclear zinc complex **3** crystallizes in the monoclinic space group C2/c. The molecule has a C₂ symmetry axis. As shown in Fig. 4, the Zn1 cation locates on a two-fold axis and adopts a distorted tetrahedral geometry with the metal centre chelated by two bidentate bisanilido ligands. The N₁–Zn1–N₂ bite angle is 99.4(2)°. The Zn2 and Zn2#1 (#1 - x, y, -z + 1/2) ions are five-coordinated and display the slightly distorted trigonal–bipyramidal geometry with the equatorial plane defined by the N1, N2, and C24 atoms, and the O1 and O2 atoms in the axial positions. The mean deviation of the Zn2 ion from the equatorial plane is only 0.0025 Å. The angles in the equatorial plane range from

93.2(2)° to 134.1(4)°, and the axial Zn2–O bonds subtend an angle of 155.21(17)°. The Zn2–N1 (2.118(5) Å) and Zn2–N2 (2.130(6) Å) bond lengths are slightly longer than the corresponding Zn1–N bond lengths (Zn1–N1: 2.009(5) Å; Zn1–N2: 2.040(5) Å). The Zn2–O1 and Zn2–O2 distances are 2.387(5) and 2.441(5) Å, respectively, indicating the weak coordination interaction between the zinc atom and the oxygen atoms in the methoxyl groups. The Zn–C bond length of 1.980(8) Å is in the normal range of the corresponding reported values (1.85–2.01 Å for the distances of Zn alkyl bonds) [17]. The Zn–Zn separation distance is 2.7684(10) Å, indicative of strong metal–metal interaction. The dihedral angle between the ring Zn1/Zn2/N1/N2 and the ring Zn1/Zn2A/N1A/N2A is 69.2°. There also exist π–π interactions between the two methoxyl substituted phenyl rings with the separation distances 3.0542 Å (distance between the ring C17/C18/C19/C20/C21/C22 and the ring C17A/C18A/C19A/C20A/C21A/C22A) and 3.6409 Å (distance between the ring C10/C11/C12/C13/C14/C15 and the ring C10A/C11A/C12A/C13A/C14A/C15A), respectively.

4. Conclusions

In conclusion, a new adduct *ortho*-C₆H₄F[CH(NHC₆H₄OMe-2)]₂ has been synthesized and characterized. Furthermore, an efficient and new method has been found for the synthesis of anilido-imine compound *ortho*-C₆H₄(2-OMeC₆H₄)(CH=NC₆H₄OMe-2). The packing of **1** was stabilized by C–H...O, C–H...N, C–H...F and N–H...O hydrogen bonds. The packing of **2** was stabilized by C–H...O and N–H...N hydrogen bonds. The novel trinuclear zinc complex **3** was obtained from the reaction of ZnEt₂ with *ortho*-C₆H₄(2-OMeC₆H₄)(CH=NC₆H₄OMe-2) by alkane elimination along with the alkylation of the imino group of the ligand. The trinuclear zinc complex **3** represents a

rare example of zinc alkyl derivative stabilized by two bianionic ONNO tetradentate ligands in four to five coordination mode.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.crci.2013.09.005>.

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