C. R. Chimie 17 (2014) 377–385

Contents lists available at ScienceDirect

Comptes Rendus Chimie

www.sciencedirect.com

Full paper/Mémoire

A new anilido-imine compound containing *o*-OMe-anilinyl 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

ARTICLE INFO

Article history:
Received 11 May 2013
Accepted after revision 10 September 2013
Available online 13 February 2014

Keywords:
Anilido-imine compound
Crystal structure
Schiff bases
Supramolecular chemistry
Zinc complexes

ABSTRACT

A new compound, *ortho*-$C_6H_4F[CH(NHC_6H_4OMe\text{-}2)_2]$, **1**, was obtained with *ortho*-flurobenzaldehyde and 2-methoxyaniline as the starting materials. Compound **1** was readily converted into *ortho*-$C_6H_4(2\text{-}OMeC_6H_4)(CH{=}NC_6H_4OMe\text{-}2)$ **2** after treatment with 1 equiv of *n*-BuLi. Treatment of compound **2** with 1.5 equiv of $ZnEt_2$ 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.

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-diketiminate (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*-fluorobenzaldehyde 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-anilinyl, 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*-$C_6H_4F(CH{=}NC_6H_4OMe\text{-}2)$ with *ortho*-flurobenzaldehyde and 2-methoxyaniline as the starting materials according to the literature [1]. However, a new compound **1** with formula *ortho*-$C_6H_4F[CH(NHC_6H_4OMe\text{-}2)_2]$ 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 phenylmethanediamine. Furthermore, compound **1** was readily converted

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

1631-0748/$ – see front matter © 2013 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.
http://dx.doi.org/10.1016/j.crci.2013.09.005

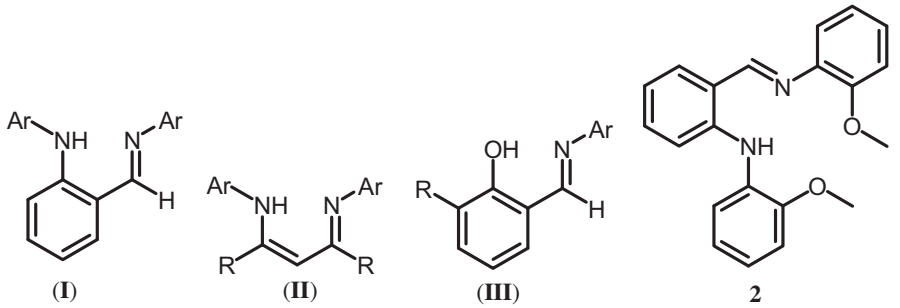
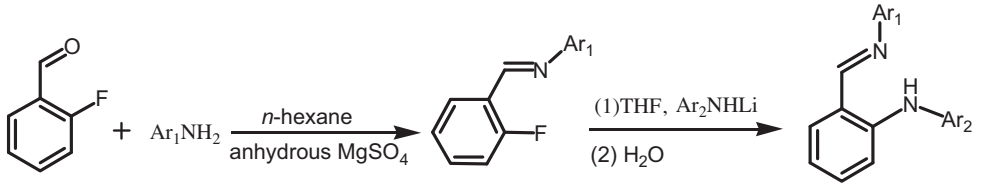


Fig. 1. Molecular structure of anilido-imine (**I**), β-diketiminate (**II**), salicylaldiminato (**III**) and object compound (**2**).



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-anilinyl 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. ^{1}H 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-$C_6H_4F[CH(NHC_6H_4OMe\text{-}2)_2]$ (1)

A mixture of *ortho*-flurobenzaldehyde (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 × 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 $C_{21}H_{21}FN_2O_2$ (352.4): C 71.57, H 6.01, N 7.95. Found: C 71.58, H 5.91, N 7.95%. ^{1}H NMR (300 MHz, DMSO-d_6, 298 K): δ = 3.74 (s, 3H, OCH_3), 3.80 (s, 2 × 3H, OCH_3), 4.67 (br, 2H, ArN*H*), 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, DMSO-d_6, 298 K): δ = 55.1 (OCH_3), 55.5 (OCH_3), 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}): υ 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-$C_6H_4(2\text{-}OMeC_6H_4)(CH{=}NC_6H_4OMe\text{-}2)$ (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*-$C_6H_4F[CH(NHC_6H_4OMe\text{-}2)_2]$ (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 × 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 $C_{21}H_{20}N_2O_2$ (332.4): C 75.88, H 6.06, N 8.43. Found: C 75.84, H 6.04, N 7.97%. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 3.90 (s, 2 × 3H, OCH_3), 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