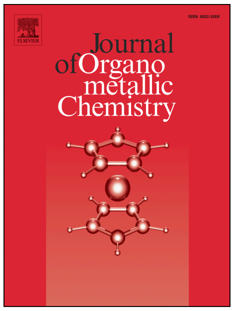

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Multinuclear Zn(II)-arylhydrazone complexes as catalysts for cyanosilylation of aldehydes

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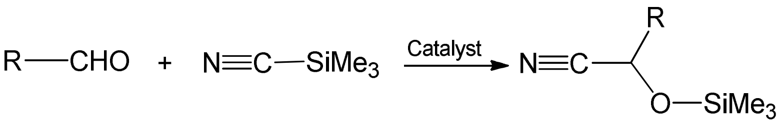
This paper is dedicated to to the 65th anniversary of INEOS and the 120th anniversary academician Alexander N. Nesmeyanov

Abstract: Three known multinuclear Zn(II)-arylhydrazone complexes, $[Zn\{(CH_3)_2SO\}(H_2O)(L^1)]$ (**1**), $[Zn_2(CH_3OH)_2(\mu\text{-}L^2)_2]$ (**2**) and $[Zn_4(\mu\text{-}OH)_2(1\kappa O{:}2\kappa O\text{-}HL^3)_4(\kappa O\text{-}HL^3)_2(H_2O)_4]$ (**3**) were prepared upon reaction of $ZnCl_2$ or $Zn(CH_3COO)_2{\cdot}2H_2O$ with 3-(2-(2-hydroxy-4-nitrophenyl) hydrazineylidene) pentane-2,4-dione (H_2L^1), 3-(2-(2-hydroxyphenyl)hydrazineylidene)pentane-2,4-dione (H_2L^2) and 2-(2-(2,4-dioxopentan-3-ylidene)hydrazineyl)benzoic acid (H_2L^3), respectively, in methanol solution. Compounds **1−3** were tested as catalysts for the cyanosilylation reaction of a diversity of both aliphatic and aromatic aldehydes with trimethylsilyl cyanide yielding the corresponding cyanohydrin trimethylsilyl ethers in high yields (72−98 %) in methanol and at room temperature.

Keywords: Mono-, di and tetranuclear Zn(II) complexes; catalysis; cyanosilylation of aldehydes

1. Introduction

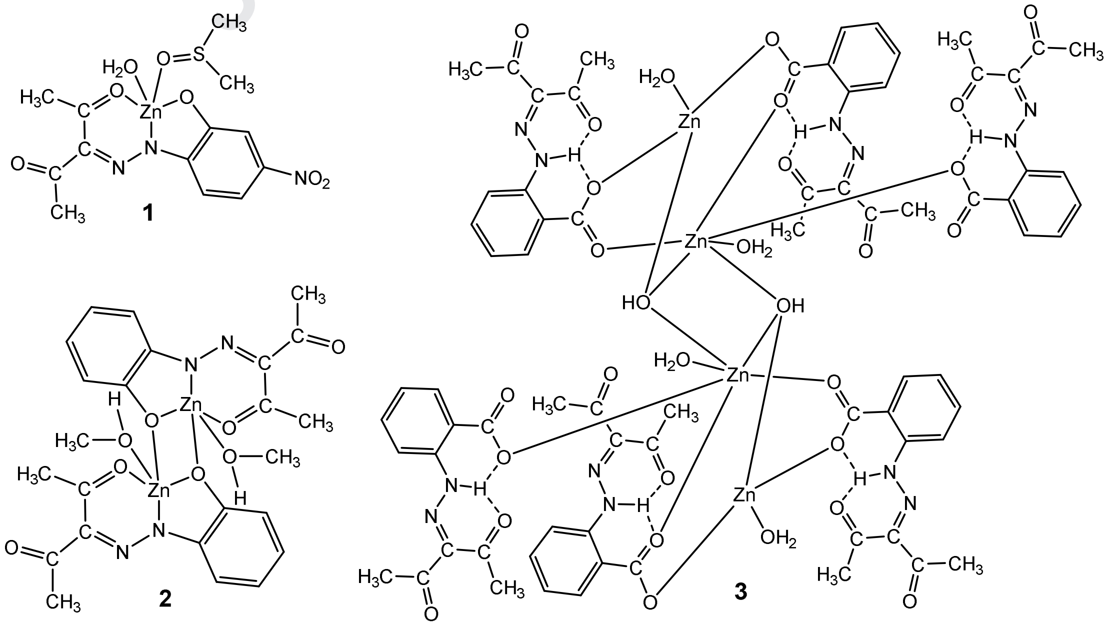
Cyanohydrins are well-known synthetic intermediates for the synthesis of α-hydroxy acids, α-hydroxyketones, α-aminonitriles, β-hydroxyamines, β-aminoalcohols, etc., which are also found as components of pharmaceuticals [1,2]. In order to avoid the volatile and extremely toxic HCN in the synthesis of cyanohydrins, the cyanation of aldehydes or ketones with trimethylsilyl cyanide (TMSCN) as the cyanide source, is a much-explored reaction (Scheme 1).



Scheme 1. Cyanosilylation of aldehydes.

In the absence of any catalyst, the reaction of benzaldehyde with TMSCN shows a limited conversion of 13 or 18 % after 3 or 14h [3,4], respectively, at room temperature. Thus, a great number of organo- and metal catalysts have been applied in order to improve the reaction yield, for example, 1,1,3,3-tetramethylguanidine [5], $P(RNCH_2CH_2)N$ [6], *N*-methylmorpholine *N*-oxide [7], *N*-heterocyclic carbenes [8,9], tetraethylammonium 2-(*N*-hydroxycarbamoyl)benzoate [10], LiCl and $LiClO_4$ [11−13], $MgBr_2·Et_2O$ [14], Mg-Li bimetallic complex [15], $Yb(CN)_3$ [16], $Yb(OTf)_3$ [17], $Cu(OTf)_2$ [18], ZnI_2 [19], KCN:18-crown-6 [20], R_2SnCl_2 an Sn-montmorillonite [21,22], BF_3 [23], $VO(OTf)_2$ [24], $InBr_3$ [25], $FeCl_3$ [26], $Zr(KPO_4)_2$ [27], NbF_5 [28], $Fe(Cp)_2PF_6$ [29], Cu(II)-arylhydrazones [30−32], lead(II)-3-aminopyrazine-2-carboxylate [33], lanthanide-containing polyoxometalates intercalated layered double hydroxides [34], supported ionic liquid [35], metal organic frameworks (MOF's) [36−41], etc. Most of these catalysts require harmful solvents, heating, prolonged reaction times, provide rather modest yields, or recover and reuse of catalysts are difficult. Therefore, the search the efficient catalyst for cyanosilylation of aliphatic and aromatic aldehydes with TMSCN in high yields, under mild reaction conditions, still remains a challenge in the field of current organic synthesis.

As other transition metals, zinc complexes have also been used as catalysts in organic synthesis [42]. According to the mechanism of Zn(II)-catalyzed transformation of aldehydes or ketones, the coordination of the oxygen atom of carbonyl group to metal centre increases the electrophilic character of carbon atom at the C=O group of aldehyde or ketone towards the nucleophilic attack by the second substrate [43]. Thus, Zn(II) complexes are able to activate C=O bonds in carbonyl compounds as alternative catalysts instead of expensive Zr, In, V, Ln, etc. based metal catalysts. Inspired by the previously obtained positive results with Zn(II)-arylhydrazone complexes in the Henry reaction by our group [44], herein we expand the catalytic potential of the complexes $[Zn\{(CH_3)_2SO\}(H_2O)(L^1)]$ (**1**), $[Zn_2(CH_3OH)_2(\mu\text{-}L^2)_2]$ (**2**) and $[Zn_4(\mu\text{-}OH)_2(1\kappa O{:}2\kappa O\text{-}HL^3)_4(\kappa O\text{-}HL^3)_2(H_2O)_4]$ (**3**) towards the cyanosilylation of aliphatic and aromatic aldehydes with TMSCN under mild conditions.



Scheme 2. Schematic representations of complexes **1−3** [44,45].

3. Experimental

3.1. Materials and instrumentation

All the chemicals were ordered from commercial sources (Aldrich) and used as received. H_2L^{1-3} and **1−3** were synthesized according to the reported procedures [42,43]. The ^{1}H NMR spectra were recorded at room temperature on a Bruker Avance II + 300 (UltraShield^{TM} Magnet) spectrometer operating at 300.130 MHz for proton. The chemical shift is described in ppm using tetramethylsilane as the internal reference.

3.2. Catalytic activity studies

In a typical cyanosilylation procedure, the solvent (CH_2Cl_2, THF or anhydrous MeOH; 2 mL) was added to a flask which contained the catalyst (**1−3**) (1−6 mol%), aldehyde (1.0 mmol) and trimethylsilyl cyanide (1.2 mmol), the solution was stirred continuously and the progress of the reaction was monitored by TLC. After a certain time, the solvent was removed, 3 mL water was added to the residue and extracted with diethyl ether (3×10 mL). After evaporation of diethyl ether under vacuum, the extract was analyzed by ^{1}H-NMR spectroscopy in $CDCl_3$, to evaluate the yield of the reaction products [46−48].

3. Results and discussion

Our initial experiments were performed using **1−3** as catalysts (Scheme 2), benzaldehyde and TMSCN as model coupling partners in protic (methanol) and aprotic (1,2-dichloromethane and THF) solvents. The results presented in Table 1 indicate the significant influence of the solvent polarity on the yield of 2-phenyl-2-((trimethylsilyl)oxy)acetonitrile. Thus, the reaction is much efficient in the protic MeOH solvent, moreover, **1−3** show a much high solubility than in CH_2Cl_2 or THF (entries 1−9, Table 1). In comparison with the mononuclear **1** and dinuclear **2** complexes, the tetranuclear **3** is the most efficient catalyst (on a molar basis) for the cyanosilylation, to give 2-phenyl-2-((trimethylsilyl)oxy) acetonitrile in *ca.* 80% yield in MeOH (Table 1, entry 9) in 16 h using 5 mol% of the catalyst. The high catalytic activity of **3** can eventually be associated to the acidic protons of the bridged hydroxyl groups, where the −OH group(s) can play a H-bond donor role in the activation of the C=O group of benzaldehyde (see below).

Free H_2L^3 bearing the −COOH group on the aromatic moiety afforded 2-phenyl-2-((trimethylsilyl)oxy)acetonitrile in 26% yield in methanol (entry 18, Table 1). When using $ZnCl_2$ or $Zn(CH_3COO)_2{\cdot}2H_2O$ as the catalysts, only 42 or 46 % yield was observed in MeOH (entries 19 and 20, Table 1), which suggests the cooperative actions of coordination (by metal centre) and weak interactions (by ligand) in the addition of CN into benzaldehyde (see below). A low yield of 2-phenyl-2-((trimethylsilyl)oxy)acetonitrile was under either catalyst-free or solvent-free conditions (entries 21-26). After checking the catalytic activities of **1−3**, H_2L^{1-3} and Zn(II) salts, **3** and methanol were chosen as preferable catalyst and solvent, respectively, for further studies.

Table 1. Selection of catalyst for the cyanosilylation of benzaldehyde with TMSCN.[a.]

Entry	Catalyst	Time (h)	Catalyst amount (mol%)	Solvent	Yield[b] (%)
1	**1**	16	5	CH_2Cl_2	36
2	**2**	16	5	CH_2Cl_2	34
3	**3**	16	5	CH_2Cl_2	38
4	**1**	16	5	THF	37
5	**2**	16	5	THF	36
6	**3**	16	5	THF	39
7	**1**	16	5	MeOH	66
8	**2**	16	5	MeOH	66
9	**3**	16	5	MeOH	80
10	H_2L^1	16	5	CH_2Cl_2	16
11	H_2L^2	16	5	CH_2Cl_2	15
12	H_2L^3	16	5	CH_2Cl_2	17
13	H_2L^1	16	5	THF	17
14	H_2L^2	16	5	THF	16
15	H_2L^3	16	5	THF	15
16	H_2L^1	16	5	MeOH	24
17	H_2L^2	16	5	MeOH	22
18	H_2L^3	16	5	MeOH	26
19	$ZnCl_2$	16	5	MeOH	42
20	$Zn(CH_3COO)_2\cdot 2H_2O$	16	5	MeOH	46
21	-	48	-	CH_2Cl_2	17
22	-	6 days	-	CH_2Cl_2	45
23	-	24	-	THF	14
24	-	16	-	MeOH	22
25	-	16	-	-	13
26	-	24	-	-	20

[a] Reaction conditions: solvent (2 mL), TMSCN (1.2 mmol) and benzaldehyde (1.0 mmol), in air at room temperature. [b] Determined by ^1H NMR.

Shortening the reaction time from 16 h to 1 h results in a significant yield decrease from 80 to 63 % (entries 1-5, Table 2), but shortening to 3h leads to almost the same yield as after 16h (entry 3 *versus* entry 5). Hence, 3h is the most adequate reaction time. When the catalyst loading increased from 1.0 mol% to 4.0 mol%, the yield of product increased from 58% to 79 % (entries 6-9, Table 2), respectively, but when the catalyst loading increased further (to reach 6 mol%), the yield increased by only 0.1 % (entry 11, Table 2). Lowering the temperature to 15 °C led to an yield decrease (entry 12, Table 2), while the increase of temperature (up to 55 °C) has only a small effect on the yield (entries 13−15, Table 2) and hence room temperature was typically used.

Table 2. Evaluation of reaction conditions of cyanosilylation of benzaldehyde with TMSCN catalyzed by **3**.[a.]

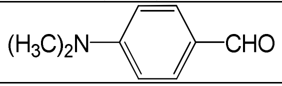
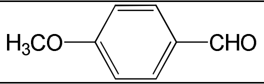
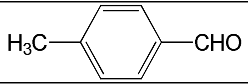
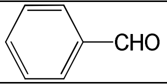
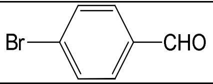
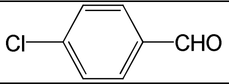
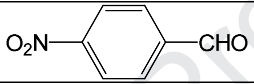
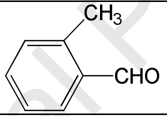
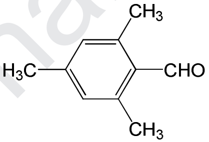
Entry	Time (h)	Catalyst amount (mol%)	*T* (˚C)	Yield[b] (%)
1	1	5	25	63
2	2	5	25	76
3	3	5	25	79
4	5	5	25	80
5	16	5	25	80
6	3	1	25	58
7	3	2	25	65
8	3	3	25	78
9	3	4	25	79
10	3	5	25	79
11	3	6	25	79
12	3	4	15	73
13	3	4	35	80
14	3	4	45	80
15	3	4	55	81

[a] Reaction conditions: MeOH (2 mL), TMSCN (1.2 mmol) and benzaldehyde (1.0 mmol), in air. [b] Determined by ^{1}H NMR.

The activities of catalyst **3** for other aldehydes in TMSCN reactions were compared under the optimized reaction conditions. The corresponding derivatives of cyanohydrin were generated in yields between 72 and 98 % (Table 3). In the case of aliphatic aldehydes, the yields were rather high (in the 93-98% range) and decreased with an increase of the chain length (entries 1-5, Table 3). For instance, propionaldehyde gave a higher yield than the other longer aliphatic aldehydes. Under the same conditions, the reaction of aromatic aldehydes with TMSCN afforded the cyanohydrin trimethylsilyl ethers in a lower yield (72−83%, entries 6-14, Table 3). Aromatic aldehydes with *para* electron-withdrawing substituents (such as −Br, −Cl or $–NO_2$) revealed the highest reactivities (entries 10-12, Table 3) as compared to those having electron-donor substituents [$−CH_3$, $−OCH_3$ or $−N(CH_3)_2$] (entries 6−8, Table 3). Both sterically hindered 2-methylbenzaldehyde and 2,4,6-trimethylbenzaldehyde gave the corresponding cyanohydrin trimethylsilyl ethers in relative low yields, 74.1 and 71.8%, respectively (entries 13 and 14, Table 3).

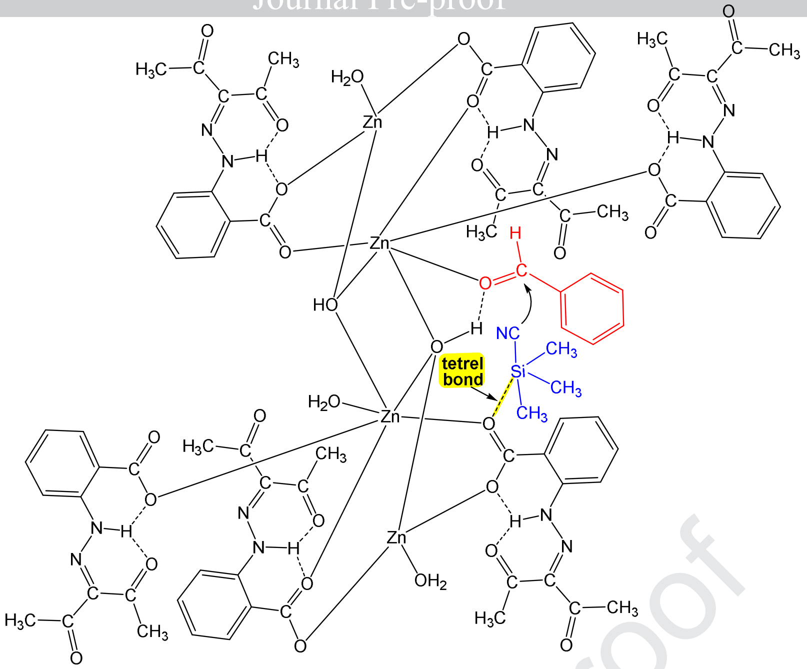
A comparison of the activity of our catalyst **3** with other reported catalytic systems for the cyanosilylation of benzaldehyde with TMSCN shows several advantages. For example: *i*) **3** shows a higher catalytic activity (79%) in methanol medium in comparison to a Zn(II)-MOF catalyst (32%) in CH_2Cl_2 [49] and a Cu(II) coordination polymer (27%) in *n*-pentane [50]; *ii*) a shorter reaction time (3 h) and room temperature are required in our system in comparison to the higher (40 ^oC) [50] or lower (-50 ^oC) [51] temperatures, and a longer reaction time (96 h) [52].

Table 3. Addition of TMSCN to aliphatic and aromatic aldehydes catalysed by catalyst **3** in methanol.[a.]

Entry	Substrate	Yield[b] (%)
1	CH_3CH_2CHO	98
2	$CH_3(CH_2)_2CHO$	97
3	$CH_3(CH_2)_3CHO$	96
4	$CH_3(CH_2)_4CHO$	96
5	$CH_3(CH_2)_5CHO$	93
6		76
7		77
8		78
9		79
10		80
11		81
12		83
13		74
14		72

[a] Reaction conditions: 4 mol% of catalyst **3**, MeOH (2 mL), TMSCN (1.2 mmol) and aldehyde (1.0 mmol); reaction time: 3 h. [b] Determined by ^{1}H NMR.

The mechanism of cyanosilylation reaction should be similar to those proposed for other metal complexes catalyzed systems, involving activation, upon coordination to the metal centre, of the aldehyde towards nucleophilic attach by TMSCN [1]. In our system, the catalytic transformation possibly can be assisted by cooperation of hydrogen bonding (provided by ligand and MeOH) with coordination, with an increase of the electrophilic character of carbon atom at the C=O group of benzaldehyde towards the nucleophilic addition of the C≡N moiety, also with the support of a tetrel bonding between the Si atom of TMSCN and a carboxylate oxygen of a ligand (Scheme 3) [1,53,54]. This would be followed by migration of the silyl group to the oxygen and subsequent liberation of the cyanohydrin trimethylsilyl ether.



Scheme 3. Proposed cooperation of coordination and noncovalent interactions in the postulated intermediate.

4. Conclusions

Three previously reported Zn(II)-arylhydrazone complexes [44,45] have been prepared and used as catalysts in the cyanosilylation of both aromatic and aliphatic aldehydes with TMSCN. On account of the acidic proton(s) of the bridged hydroxyl group(s), the catalytic activity of complex **3** (tetranuclear) is higher than those of **1** (mononuclear) and **2** (dinuclear) in methanol at room temperature, producing cyanohydrin trimethylsilyl ethers in high yields (72−98%) in 3 h. As substrates, both aliphatic and aromatic aldehydes are employed effectively, and the electron-donor or withdrawing character of a substituent in the *para* position of the aromatic aldehydes has an inhibiting or promoting effect, respectively, on the reaction yield.

Not only a conventional coordination bond, but also hydrogen and tetrel noncovalent bonds are postulated in the proposed mechanism for the addition of TMSCN to the aldehyde. Further studies focusing on the modification of arylhydrazone ligands in the design of coordination compounds and their use as catalysts for cyanosilylation and other C−C coupling reactions promoted by noncovalent interactions are currently under study and will be reported in due course.

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Highlights

► Multinuclear zinc(II) complexes with arylhydrazones of active methylene compounds

► A tetranuclear zinc(II) complex shows high catalytic activity in cyanosilylation of aldehydes

► The yield of cyanohydrin trimethylsilyl ethers depends on the amounts of catalyst and nature of solvents

Conflicts of Interest: The authors declare no conflicts of interest.