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Alkoxo bridged heterobimetallic $Co^{III}Sn^{IV}$ compounds with face shared coordination octahedra: Synthesis, crystal structure and cyanosilylation catalysis[☆]

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The self-assembly reaction of the Schiff base *N,N'*-ethylenebis(2-hydroxyacetophenoneimine) (H_2L), $CoCl_2{\cdot}6H_2O$ and $[SnPh_2Cl_2]$ led to the alkoxo-bridged heteroorganometallic $Co^{III}Sn^{IV}$ complex $[\{SnPhCl_2\}(1\kappa O^2{:}2\kappa O^2N^2\text{-}\mu\text{-L})(\mu\text{-OMe})\{CoPh\}]{\cdot}CH_3OH{\cdot}H_2O$ (**1**) or $[\{SnPhCl_2\}(1\kappa O^2{:}2\kappa O^2N^2\text{-}\mu\text{-L})(\mu\text{-OEt})\{CoPh\}]$ (**2**) in MeOH or EtOH, respectively. The structures of these complexes are authenticated by single crystal X-ray diffraction analyses. They are derived from an intermetallic (Sn to Co) phenyl shift, leading to face-shared distorted octahedral coordination geometries. The complexes were tested as homogeneous catalysts for the solvent-free cyanosilylation reaction of benzaldehyde with trimethylsilyl cyanide (TMSCN) under low power microwave irradiation at 50°C. They exhibited a high catalytic activity, yielding (for catalyst **1**) up to 93% of the cyano-derivative from benzaldehyde in 90 minutes.

1. Introduction

Salen [*N,N'*-ethylenebis(salicylaldimine)] or substituted salens are extensively utilized Schiff bases for the design of versatile heterometallic compounds which are important in the field of crystal engineering [1-3], magnetism [4-6], catalysis [7-9] and biology [10,11]. Such a ligand can stabilize heterometallic systems with combinations of 3d-s, 3d-3d, 3d-p, 3d-f metals, etc [1-16]. Even heterometallic compounds with more than two metal combinations are also known, such as heterotri- [5,12-15] or heterotetrametallic [16] compounds. The diversity has been further enhanced by the 3d metal-tin(II/IV) compounds [1], with attractive crystal structures, obtained under open atmosphere [1,17-20]. In many cases, the isolated products are uncommon, being dependent on several factors (ligand, metal oxidation state, solvents, etc.). For example, heterobimetallic Cu^{II}/Ni^{II}-Sn^{IV} or Cu^{II}-Sn^{II} systems of substituted salens [*N,N'*-ethylenebis(3-methoxy/ethoxy salicylaldimine)] were isolated in different forms, such as a simple adduct, cocrystals, cocrystal salts or complex salts [17,18]. It becomes further interesting when an unsubstituted salen was reacted with $MCl_2.xH_2O$ (M = Cu, Ni, Co) and $[SnPh_2Cl_2]$ in alcohol [19]. The derived Ni/Cu-Sn products are stabilized by Ni/Cu$\cdots\pi$(Ph)–Sn interaction, whereas a 2,1-phenyl shift resulted in a methoxido bridged heteroorganobimetallic Co(Ph)-Sn(Ph) compound. Such a shift occurs only after the aerobic oxidation Co(II) to Co(III) [19], as indicated by theoretical calculations. Attempts to isolate from ethanol the analogous ethoxido bridged derivative resulted in the organometallic phenylcobalt(III) compound. Further alteration of the solvent from alcohol to acetone produced the mixed valence organometallic $Co(III)_2Co(II)$ compound [20], indicating the relevant role of solvent in the unexpected product formation. Inspired by our previous works and with the aim to further explore such systems, we have now used the slightly modified Schiff base *N,N'*-ethylenebis(2-hydroxyacetophenoneimine) (H_2L) which was reacted with $CoCl_2{\cdot}6H_2O$ and $[SnPh_2Cl_2]$ in methanol to obtain the methoxido bridged heteroorganobimetallic Co^{III}(Ph)-Sn^{IV}(Ph) compound $[\{SnPhCl_2\}(1\kappa O^2{:}2\kappa O^2N^2\text{-}\mu\text{-L})(\mu\text{-OMe})\{CoPh\}]{\cdot}CH_3OH{\cdot}H_2O$ (**1**). In addition, the reaction in ethanol produces the targeted ethoxido bridged analogue $[\{SnPhCl_2\}(1\kappa O^2{:}2\kappa O^2N^2\text{-}\mu\text{-L})(\mu\text{-OEt})\{CoPh\}]$ (**2**). The successful isolation of the ethoxido bridged system **2** from H_2L is an interesting addition to this rare class of

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[☆] Dedicated to Prof. Elena Shubina, on the occasion of her 70th birthday, as a recognition of her achievements towards the development of Science.

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$Co^{III}Sn^{IV}$ systems with three oxido bridges (one alkoxido and two phenoxidos).

On the other hand, cyanosilylation is an important classic organic C–C bond forming reaction to synthesize α-silyloxy nitrile species from aldehydes or ketones [21-23]. Such a nitrile can provide a useful protective group in organic synthesis or can be hydrolyzed to produce valuable functionalized organic derivatives such as cyanohydrins, α-hydroxycarboxylic acids or β-amino alcohols which are important in synthetic chemistry and biological processes [24-28]. Several homo- and heterogeneous systems [21-34] including compounds containing cobalt [29-31] or tin metal ions were utilized to efficiently catalyze the reaction [32-34]. Therefore, the possibility of a heterometallic CoSn complex to act as an effective catalyst can be anticipated. However, to our knowledge, such a type of system has never been investigated in this reaction. Hence, we have now tested the catalytic activity of the above mentioned heteroorganometallic $Co^{III}Sn^{IV}$ compounds in the cyanosilylation reaction of benzaldehyde and substituted forms.

2. Experimental section

2.1. Materials and physical methods

All the reagents and solvents were purchased from commercial sources and used as received. The Schiff base H_2L was synthesized by condensing 2-hydroxyacetophenone with 1,2-ethylendiamine following a similar procedure to that used for the synthesis of salen [19]. NMR spectra of H_2L were obtained on a Bruker 400 MHz spectrometer using tetramethylsilane $[Si(CH_3)_4]$ as internal reference. FT-IR spectra were recorded in the 400–4000 cm^{-1} region on a Bruker Vertex 70 spectrophotometer with samples as KBr disks; abbreviations: s = strong, m = medium, and w = weak. Elemental analyses were performed on a Perkin-Elmer 2400 II analyzer. Mass spectra of sample solution in methanol (for **1**) or ethanol (for **2**) were acquired on a Bruker HCT quadrupole ion trap equipped with an electrospray ion source using the following typical instrumental parameters: solution flow rate, 2.5 μL/min; ESI needle spray voltage, +4 kV; capillary exit voltage, −129 V; nebulizer gas pressure, 8 psi; dry gas flow rate, 4 L/min; dry gas temperature, 250°C; octopole RF amplitude, 187 Vpp. The spectra were recorded in the range 100 – 1500 Da. Spectra typically correspond to the average of 20–35 scans. Catalytic reactions were carried out using a FISONS Instruments Anton Paar Monowave 300 microwave synthesis reactor at 50°C.

2.2. Synthesis of $[\{SnPhCl_2\}(1\kappa O^2N^2,2\kappa O^2\text{-}\mu\text{-}L)(\mu\text{-}OMe)\{CoPh\}]$ (**1**)

To a methanol suspension (15 mL) of H_2L (0.074 g, 0.25 mmol) was added a methanol solution (2 mL) of $CoCl_2{\cdot}6H_2O$ (0.060 g, 0.25 mmol) to obtain an orange solution. Subsequent addition of a methanol solution (3 mL) of $[SnPh_2Cl_2]$ (0.086 g, 0.25 mmol) to that reaction mixture produced a dark red solution which was kept at room temperature for slow evaporation. Within 1 d, the formed red crystals, suitable for X-ray diffraction analysis, were collected by filtration and washed with cold methanol. Yield: 0.148 g (76%). $C_{32}H_{37}Cl_2N_2O_5CoSn$ (778.20): calcd. C 49.39, H 4.79, N 3.60%; found. C 49.51, H 4.83, N 3.59%. IR data (KBr, cm^{-1}): ν(C=N), 1581s. ESI-MS: $[Na{\cdot}\mathbf{1}{\cdot}MeOH]^+$ [calcd. 783.02 (100%); found 782.96]; $[HLCoPh]^+$ [calcd. 431.12; found 431.10].

2.3. Synthesis of $[\{SnPhCl_2\}(1\kappa O^2N^2,2\kappa O^2\text{-}\mu\text{-}L)(\mu\text{-}OEt)\{CoPh\}]$ (**2**)

To an ethanol suspension (15 mL) of H_2L (0.074 g, 0.25 mmol) was added an ethanol solution (2 mL) of $CoCl_2{\cdot}6H_2O$ (0.060 g, 0.25 mmol) to obtain an orange solution. Addition of an ethanol solution (3 mL) of $[SnPh_2Cl_2]$ (0.086 g, 0.25 mmol) to that reaction mixture resulted a red solution along with an unidentified brown solid precipitate. After removing the solid product by filtration, the obtained solution was kept at room temperature for slow evaporation. Within 6 h, the formed red crystals, suitable for X-ray diffraction analysis, were collected by filtration and washed with cold ethanol. Yield: 0.080 g (41%). $C_{32}H_{33}Cl_2N_2O_3CoSn$ (742.17): calcd. C 51.79, H 4.48, N 3.77%; found. C 51.75, H 4.51, N 3.73%. IR data (KBr, cm^{-1}): ν(C=N), 1590s. ESI-MS: $[Na(LCoPh)_2]^+$ [calcd. 883.21 (100%), found 883.06]; $[HLCoPh]^+$ [calcd. 431.12, found 431.10]; $[Na(LCoPh)]^+$ [calcd. 453.01; found 453.10].

2.4. Crystal structure determination

X-ray quality crystals of **1** and **2** were immersed in cryo-oil and mounted in a Nylon loop and measured at 298 K. Intensity data were collected using a Bruker APEX II SMART CCD diffractometer with graphite monochromated Mo-Kα (λ 0.71073) radiation. Cell parameters were obtained with Bruker SMART [35] software and refined with Bruker SAINT [35] on all the observed reflections. Absorption corrections were made by the multi-scan method (SADABS) [35]. Structures were solved by direct methods by using the SHELXS-2014 package [36] and refined with SHELXL-2014/7 [36]. Calculations were performed using the WinGX System-Version 2014.1 [37]. Hydrogen atoms attached to carbon atoms were inserted at geometrically calculated positions and included in the refinement using the riding-model approximation. Uiso(H) were defined as 1.2 Ueq of the parent carbon atoms. Solvent molecules in the structure of **1** were highly disordered and could not be modelled; therefore, they were removed by using *PLATON* SQUEEZE routine [38]. A total void of 122 Å^3 containing 58 electrons per unit cell was found and fits well for one methanol (18 electrons) and one water molecule (10 electrons) per asymmetric unit, being consistent with the elemental analysis. Disordered phenyl (C26-C28) and ethoxido (C31 and C32) carbons in **2** were modelled by means of PART 1 and PART 2 instructions, leading to the occupancies of 57.5 and 42.5%. Least square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms were employed. Crystallographic data are summarized in Table S1 (Supplementary information, SI).

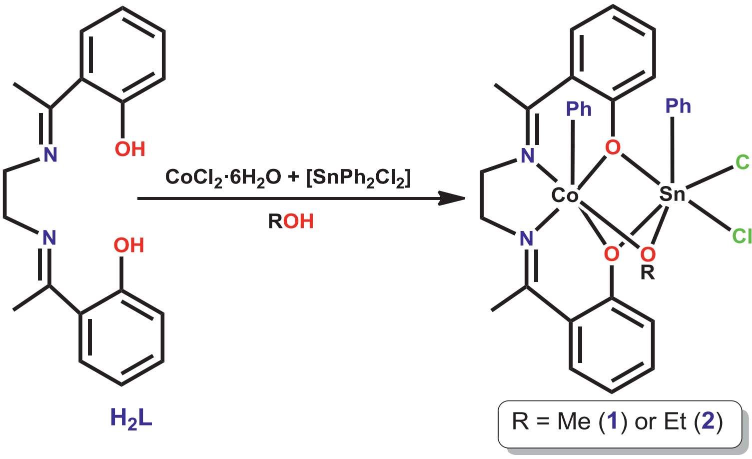
2.5. Cyanosilylation of benzaldehyde catalyzed by heteroorganometallic $Co^{III}Sn^{IV}$ complexes

A mixture of benzaldehyde (0.50 mmol), trimethylsilyl cyanide (1.0 mmol) and 1 mol% catalyst (7.8 or 7.4 mg for **1** or **2**, respectively) was placed in a Pyrex tube covered with a teflon cap and stirred at 50°C under microwave irradiation (10 W) for 90 min without any solvent. The final product was identified by ^1H NMR spectroscopy and the product yield was calculated using the same procedure as reported in the literature [23].

3. Results and discussion

3.1. Synthesis and characterization

The single compartmental Schiff base *N,N'*-ethylenebis(2-hydroxyacetophenoneimine) (H_2L) (Scheme 1) was synthesized by condensing 2-hydroxyacetophenoneimine with 1,2-ethylenediamine (2:1) in methanol following the reported procedure used for the synthesis of salen [*N,N'*-ethylenebis(salicylaldimine)] [19]. The reaction of H_2L with $CoCl_2{\cdot}6H_2O$ and $[SnPh_2Cl_2]$ in MeOH, under open atmosphere and at room temperature, produces the heteroorganobimetallic $Co^{III}Sn^{IV}$ compound $[\{SnPhCl_2\}(1\kappa O^2{:}2\kappa O^2N^2\text{-}\mu\text{-}L)(\mu\text{-}OMe)\{CoPh\}]{\cdot}CH_3OH{\cdot}H_2O$ (**1**). We have also successfully isolated



Scheme 1. Synthesis of **1** and **2**.

the analogous ethoxido bridged system [{SnPhCl$_2$}(1κO^2:2κO^2N^2-μ-L)(μ-OEt){CoPh}] (**2**) from EtOH, in contrast to our earlier study [19] when attempts to isolate the μ-OEt system resulted the mononuclear salen phenylcobalt(III) compound.

Compound **1** was isolated in good yield (76%). The reaction in ethanol (20 mL) was faster and produced immediately a solid product. From the filtrate, the compound **2** was isolated in a reasonable yield (41%). The open-air formation of the RO$^-$ bridged Co^{III}Sn^{IV} compound [R = Me (**1**) or Et (**2**)] is expected to proceed *via* the Co^{II} to Co^{III} aerial oxidation, followed by a phenyl shift from Sn^{IV} to Co^{III} in a similar way as that proved for a related salen based system [19].

In the IR spectra, compounds **1** and **2** exhibit a strong intense absorption at 1581 and 1590 cm^{-1}, respectively, due to ν(C=N), at a lower wavenumber than that (1603 cm^{-1}) of the pro-ligand H$_2$L. Both metal complexes were also characterized by elemental analyses, ESI-MS and single crystal X-ray diffraction studies.

The obtained ESI-MS (m/z, +ve mode) spectra indicate that the heterometallic form of **1** is stable, producing [Na·**1**·MeOH]$^+$ [calcd. 783.02 (100%); found 782.96], while the organocobalt(III) species [Na(LCoPh)$_2$]$^+$ [calcd. 883.21 (100%); found 883.06] is generated from **2** under the ESI-MS conditions. In addition, the mononuclear organocobalt(III) cations [HLCoPh]$^+$ (for **1** and **2**) or [Na(LCoPh)]$^+$ (for **2**) [calcd. 431.12 and 453.01; found 431.10 and 453.10, respectively] are detected.

3.2. Description of crystal structures

The crystal structures of the heteroorganobimetallic compounds [{SnPhCl$_2$}(1κO^2:2κO^2N^2-μ-L)(μ-OMe){CoPh}]·CH$_3$OH·H$_2$O (**1**) and [{SnPhCl$_2$}(1κO^2:2κO^2N^2-μ-L)(μ-OMe){CoPh}] (**2**) are shown in Fig. 1. Selected bond distances and angles are included in Table 1.

Compounds **1** and **2** are analogous but crystallize in different space groups, triclinic *P*-1 (**1**) and monoclinic *P*21/*c* (**2**). The L^{2-} Schiff base ligand chelates the transition metal cation (Co^{III}) in the expected *OO'NN'*-way and *OO'*-bridges to the {SnPhCl$_2$} unit. The bridging alkoxide (MeO and EtO in **1** and **2**, respectively) fulfills the Sn^{IV} octahedral type coordination environment as well as, together with a phenyl group, the distorted octahedral coordination geometry at Co^{III}. Interestingly, the coordination octahedra share the O$_3$ face (Fig. 2).

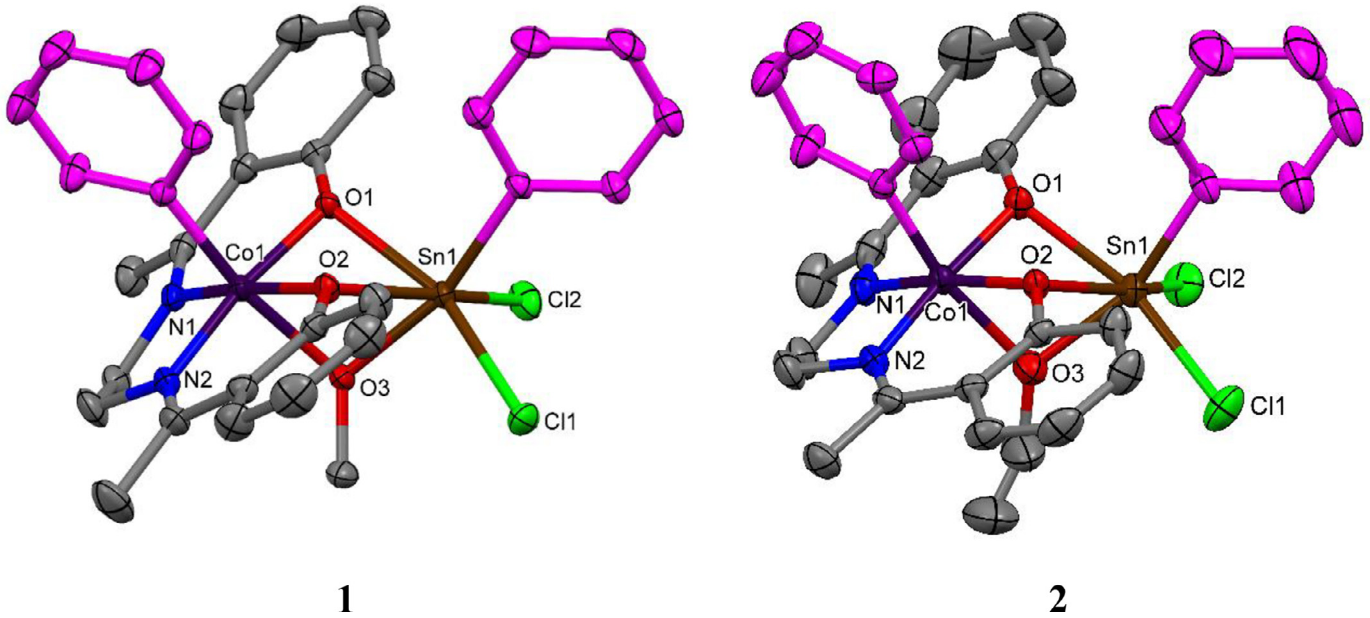
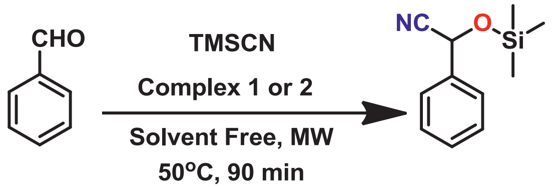


Fig. 1. Ellipsoid (30% probability) plot with partial atom labeling scheme of the crystal structure of **1** and **2**. All H-atoms, and second part of disorder atoms (only in **2**) are omitted for clarity.

Table 1
Comparison of selected bond distances (Å) and angles (°) in complexes **1** and **2**.

	1	**2**
In the ligand		
C=N	1.289(3), 1.290(3)	1.286(4), 1.294(4)
∠ Between the l.s. planes of the aromatic rings	21.46	14.34
Around the Co^{III} and Sn^{IV} ions		
$Co{-}N_{imine}$	1.8826(18), 1.8839(17)	1.880(2), 1.885(3)
$Co{-}O_{phenoxido}$	1.8939(14), 1.9048(14)	1.885(2), 1.8940(19)
$Co{-}O_{alkoxido}$	2.1255(15)	2.133(2)
$Co{-}C_{phenyl}$	1.947(2)	1.943(3)
$Sn{-}O_{phenoxido}$	2.2246(14), 2.2562(16)	2.240(2), 2.3134(19)
$Sn{-}O_{alkoxido}$	2.0391(14)	2.018(2)
$Sn{-}C_{phenyl}$	2.135(2)	2.143(3)
Sn–Cl	2.4321(12), 2.4327(9)	2.4038(9), 2.4097(10)
$\angle N_{imine}{-}Co{-}O_{phenoxido}$ (trans)	169.01(6), 172.13(6)	167.79(11), 175.40(10)
$\angle O_{alkoxido}{-}Co{-}C_{phenyl}$	170.75(7)	168.48(11)
∠Cl–Sn–Cl	98.35(3)	97.39(4)
Co···Sn	2.9552(13)	2.9895(4)
Displacement of Co from the least square N_2O_2 plane	0.137	0.120
Displacement of Sn from least square O_2Cl_2 plane	0.243	0.224
Angle between the N_2O_2 and O_2Cl_2 planes	67.56	65.31



Scheme 2. Solvent-free cyanosilylation reaction of benzaldehyde catalyzed by **1** or **2**.

Compounds **1** and **2** are engaged with three four-membered rings of the type CoO_2Sn, one five-membered CoC_2N_2 and two six-membered CoC_3NO rings (Fig. 1).

In the crystal structures of **1** and **2**, the $Co{-}N_{imine}$ and Sn–Cl bonds are the shortest and longest ones, respectively (Table 1). The $M{-}O_{phenoxido}$ and $M{-}C_{phenyl}$ bond distances around the Co^{III} are shorter than those around the Sn^{IV} metal ion (Table 1) while the $M{-}O_{alkoxido}$ bond follows the opposite trend (Table 1). Interestingly, the distance between the metal centres is slightly greater than the sum (2.65 Å) of their covalent radii, suggesting a Co···Sn interaction. Except the displacement parameter (0.137 Å *vs.* 0.120 in **1** and **2**, respectively, Table 1) of Co^{III} from the ligand N_2O_2 plane, all other geometrical parameters are similar. In fact, they are comparable to those reported earlier for phenylcobalt(III) containing $Co^{III}(Ph)Sn^{IV}(Ph)$, $Co^{III}(Ph)$ and $\{Co^{III}(Ph)\}_2Co^{II}$ compounds [19,20].

The crystal structure of both compounds are stabilized by intramolecular C_{phenyl}–H···N and C_{phenyl}–H···O contacts, in **1** involving only the Co-phenyl ligand [C20–H20···O2: $d_{D\cdots A}$ 2.915(3) Å, 117°; C24–H24···N1: $d_{D\cdots A}$ 2.995(3) Å, 111°] but in **2** involving both such rings [C20–H20···O2: $d_{D\cdots A}$ 2.916(4) Å, 118°; C24–H24···N1: $d_{D\cdots A}$ 2.972(5) Å, 115°; C30–H30···O2: $d_{D\cdots A}$ 3.185(5) Å, 122°] (Fig. S1, SI). Intermolecular C–H···Cl hydrogen bonds (H···Cl distances lower

Table 2
Cyanosilylation reaction[a] of benzaldehydes with TMSCN catalyzed by **1** and **2**.

Entry	Catalyst	Substrate	Time (min)	Amount of Catalyst (mol%)	Solvent	T (°C)	Yield[b] (%)
1	**1**	PhCHO	90	1.0	Solvent free	50	93
2	**1**	PhCHO	90	1.0	Solvent free	50	91
3	**1**	PhCHO	15	1.0	Solvent free	50	30
4	**1**	PhCHO	30	1.0	Solvent free	50	65
5	**1**	PhCHO	45	1.0	Solvent free	50	83
6	**1**	PhCHO	60	1.0	Solvent free	50	91
7	**1**	PhCHO	75	1.0	Solvent free	50	92
8	**1**	PhCHO	90	0.5	Solvent free	50	89
9	**1**	PhCHO	90	3.0	Solvent free	50	93
10	**1**	PhCHO	90	1.0	Solvent free	25	41
11	**1**	PhCHO	90	1.0	Solvent free	75	94
12	**1**	PhCHO	90	1.0	MeOH	50	85
13	**1**	PhCHO	90	1.0	DCM	50	63
14	**1**	PhCHO	90	1.0	CH_3CN	50	77
15	Blank	PhCHO	90	-	Solvent free	50	11
16	$[Ph_2SnCl_2]$	PhCHO	90	1.0	Solvent free	50	30
17	Ligand	PhCHO	90	1.0	Solvent free	50	28
18	**1**	4-NO_2PhCHO	90	1.0	Solvent free	50	98
19	**1**	4-BrPhCHO	90	1.0	Solvent free	50	94
20	**1**	4-MePhCHO	90	1.0	Solvent free	50	85
21	**1**	4-MeOPhCHO	90	1.0	Solvent free	50	78

[a] Reaction conditions, unless stated otherwise: benzaldehyde (0.50 mmol), TMSCN (1.00 mmol) and catalyst (1 mol%) at 50 °C under microwave irradiation;

[b] Calculated by ^{1}H-NMR as the number of moles of product 2-phenyl-2-((trimethylsilyl)oxy)acetonitrile per mole of aldehyde x 100.

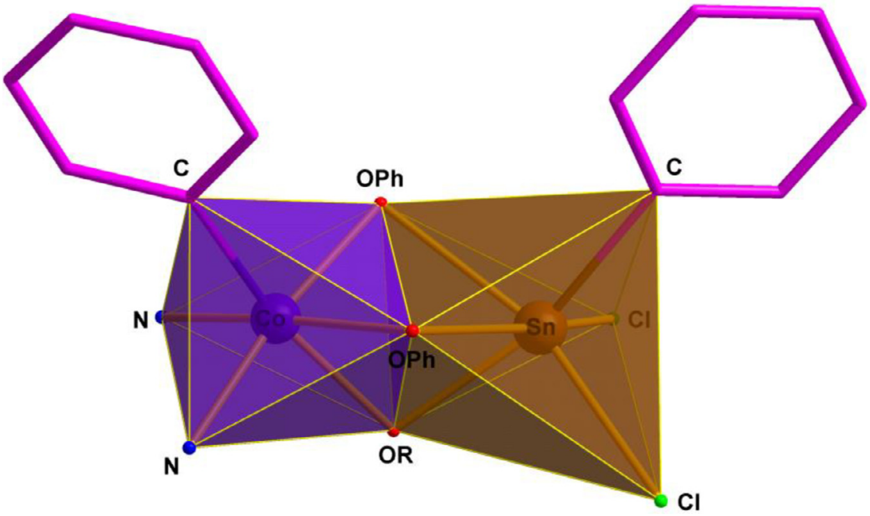


Fig. 2. Face shared organometallic octahedra in **1** and **2**. R = Me (**1**) or Et (**2**).

than 3 Å) form distinct supramolecular associates: a double 1D chain in **1** and a 2D sheet in **2** (Fig. S2, SI).

3.3. Structural search of related organometallic compounds

A structural search for the heterometallic Sn compounds (Sn with all other metals) made on the CSD (Cambridge Structural Database, ConQuest Version 2020.2.0) [39] results in 4123 hits. Limiting the search to only heterometallic CoSn, gave only 175 compounds (~4%). Another search for the Co–Ph fragment resulted in only 30 hits (phenylcobalt compounds). Restricting the search to only heterometallic-Co(Ph), gave only 4 compounds. It is thus evident that heterometallic phenylcobalt compounds have been rarely investigated, at least by crystal structure characterization. Only one heteroorganometallic compound with Co–Ph and Sn–Ph fragments has been reported, and thus complexes **1** and **2** appear to be the second and third examples of such systems.

The search for the alkoxido or phenoxido bridged transition metal-Sn systems resulted in 56 compounds, while the methoxido or ethoxido bridged systems are only 2 and 9, respectively [39]. Thus, the compound **1** is the third one having a methoxido bridge while **2** is the 10th compound with an ethoxido bridge. In addition, the number of transition metal-Sn systems with tris(oxido/alkoxido/phenoxido) is only 3.

3.4. Catalytic cyanosilylation reactions catalyzed by 1 and 2

We have tested the catalytic activity of the heteroorganometallic complexes (**1** and **2**) as homogeneous catalysts in the solvent-free cyanosilylation reaction of benzaldehyde. In this catalytic reaction, a mixture of benzaldehyde, trimethylsilyl cyanide (TMSCN) and $Co^{III}Sn^{IV}$-catalyst (**1** or **2**) was stirred under microwave irradiation (10 W) at 50°C, under solvent-free conditions (Scheme 2). The crude product mixtures were analyzed by ^1H NMR as previously described in literatures [34].

By performing the catalytic reaction using benzaldehyde (as a test compound), the complex **1** exhibits a slightly higher catalytic activity than the complex **2** (93% vs. to 91% yield, respectively). Therefore, the optimization process for the cyanosilylation of benzaldehyde by TMSCN was carried out with complex **1** as the catalyst (Scheme 2 and Table 2).

For the optimization, first we have performed the reaction in different solvents, such as MeOH, DCM and CH_3CN, as well as without any solvent. The use of MeOH, DCM and CH_3CN led to the yield of 85%, 63% and 77%, respectively (entries 12-14, Table 2). However, solvent-free conditions show the maximum product yield of 93% (entry 1, Table 2). In order to study the effect of catalyst loading, we have performed the catalytic reactions with three different catalyst amounts, *i.e.*, 0.5, 1.0 and 3.0 mol% and the obtained product yields are in the range of 89-93% (entries 1, 8 and 9, Table 2). The maximum product yield of 93% was obtained using 1.0 mol% of catalyst; when we increased the catalyst load until 3.0 mol% no yield change was observed. Thus, the optimal catalyst amount was considered as 1 mol% (relative to the aldehyde).

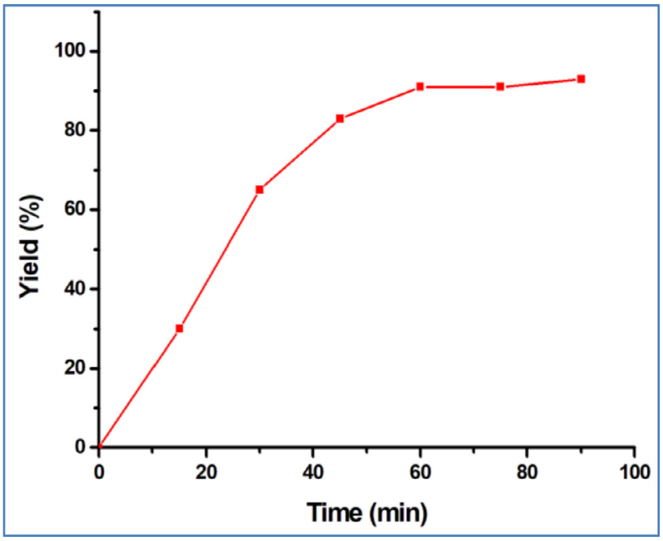


Fig. 3. Plot of yield *vs.* time for the microwave assisted solvent-free cyanosilylation reaction of benzaldehyde, catalyzed by complex **1**.

We have also studied the effect of temperature on cyanosilylation reaction. Upon performing the reaction at room temperature (25°C) only 41% of product yield was obtained (entry 10, Table 2). However, increasing the reaction temperature from 25°C to 50°C resulted in a yield increase up to 93% (entry 1, Table 2), whereas an additional increase in the temperature until 75°C led only to a very slight improvement in the reaction yield (entry 11, Table 2).

The yield *vs.* time plot for the cyanosilylation reaction of benzaldehyde and TMSCN catalyzed by **1** is presented in Fig. 3 (the maximum yield is almost reached after 60 minutes).

A blank test was undertaken without any catalyst and resulted in only 11% yield of the product yield (entry 15, Table 2). Moreover, we have also checked the cyanosilylation reaction with [Ph_2SnCl_2] and the pro-ligand H_2L and the reaction yields were 30% and 28%, respectively (entries 16 and 17, Table 2).

Thus, the optimized reaction conditions for our complexes **1** and **2** produce 93% and 91% of final product yield after 1.5 h at 50°C under microwave irradiation, respectively.

We have also studied the catalytic activity of our complex **1** towards different substituted aromatic aldehydes. The aromatic aldehydes encompassing a strong electron-withdrawing group, *i.e.*, -NO_2 or -Br, show the higher yields in the range of 94-98% (entries 18 and 19, Table 2), whereas the aldehydes having an electron-donating substituent, *i.e.*, -OMe or -Me, exhibit lower yields (78-85%, entries 20 and 21, Table 2). These performances are in concurrence with the anticipated effect of the substituent on the electrophilic character of the aldehyde (CHO) carbon to undergo attack by the cyano group of TMSCN [23].

4. Conclusion

The reactions of *N,N'*-ethylenebis(2-hydroxyacetophenoneimine) (H_2L) with $CoCl_2·6H_2O$ and [$SnPh_2Cl_2$] in an alcohol, produce the heteroorganobimetallic Co^{III}-Sn^{IV} complexes [$\{SnPhCl_2\}(1\kappa O^2N^2,2\kappa O^2\text{-}\mu\text{-L})(\mu\text{-OR})\{CoPh\}$] {R = Me (**1**) and Et (**2**)} under open atmosphere and at room temperature. A Sn^{IV}-to-Co^{III} intermetallic phenyl ligand shift is involved in the formation of these heterometallic Co(Ph)Sn(Ph) systems (**1** and **2**) and the synthetic results prove that the ethoxido (apart from the methoxido) bridge can also stabilize such systems, which was not observed [19] in the case of the analogous salen pro-ligand.

Interestingly, the complexes exhibit face-shared distorted octahedral coordination geometries and they are the second and third heterometallic compounds, reported structurally, containing the Co-Ph and Sn-Ph fragments together, as found in the CSD. In addition, compound **1** is the third transition metal-tin metal compound with a methoxido bridge, while **2** is the 10th of such metal compounds with an ethoxido bridge. All these structural surveys lead to the conclusion that **1** and **2** (along with our earlier reported related system [19]) belong to a rare family of compounds, which deserves further investigation.

The heteroorganometallic complexes **1** and **2** efficiently catalyze the added solvent-free cyanosilylation of benzaldehyde with trimethylsilyl cyanide (TMSCN) under low power microwave irradiation at 50°C. The metal centres play an important role in the reaction, acting as a Lewis acid to activate the carbonyl group of benzaldehyde (substrate) and promoting the formation of corresponding cyano product from benzaldehyde, as supported by experiments with substituted benzaldehydes. Detailed catalytic studies (such as, under microwave free conditions and mechanistic investigations of the catalytic reaction) with these complexes along with related systems are under progress. To our knowledge, a heteroorganometallic $Co^{III}Sn^{IV}$ compound, such as **1** and **2**, has never been applied in catalytic cyanosilylation reaction.

Moreover, the compounds of this study can contribute to the development of the organometallic chemistry and catalysis of mixed Co/Sn complexes. Further reactions of the types of metal salts and ligand combinations applied in this study to prepare new heterometallic complexes are underway.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2021.121949.

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