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Research paper

Cyanosilylation of carbonyl compounds catalyzed by half-sandwich (η^6-*p*-cymene) Ruthenium(II) complexes bearing heterocyclic hydrazone derivatives

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ABSTRACT

A new class of half-sandwich (η^6-*p*-cymene) ruthenium(II) complexes supported by heterocyclic hydrazone derivatives of general formula [Ru(η^6-*p*-cymene)(Cl)(L)] where **L** represents N'-((1*H*-pyrrol-2-yl)methylene) furan-2-carbohydrazide (**L^1**), N'-((1*H*-pyrrol-2-yl)methylene)thiophene-2-carbohydrazide (**L^2**) or N'-((1*H*-pyrrol-2-yl)methylene)isonicotinohydrazide (**L^3**) were synthesized. Both ligand precursors and complexes were characterized by elemental and spectral analysis (IR, UV–Vis, NMR and mass spectrometry). The molecular structures of all Ru complexes [Ru(η^6-*p*-cymene)(Cl)(L)] were determined by single-crystal X-ray diffraction as three-legged piano-stool. The Ru(II) complexes were used as catalysts for the cyanosilylation of aldehydes (aliphatic, aromatic, α,β-unsaturated and heterocyclic aldehydes) with trimethylsilyl cyanide (TMSCN). All reactions were performed at room temperature and catalytic conditions as solvents, catalyst and catalyst loading were experimentally optimized. Using 0.5 mol% of Ru catalyst **3** in Et_2O it was possible to prepare cyanosilylethers in good-to-excellent isolated yields.

1. Introduction

Cyanosilylation of aldehydes with trimethylsilyl cyanide is the unique available route to synthesize cyanohydrin derivatives through formation of carbon-carbon bonds [1]. Chiral cyanosilyl moieties are used as protective groups in organic synthesis [2]. They are optically active compounds that may be converted in a wide range of multifunctional intermediates such as α-hydroxy acids, α-amino acids, β-amino alcohols, nitroolefins, α-hydroxy esters and α-hydroxy ketones, and they for play a significant role in the synthesis of a large number of pharmaceuticals, agrochemicals and insecticides [3,4]. The synthesis of α-silyloxy nitriles involves protection of the alcohol moiety through O-silylated cyanohydrin (OTMS) that enables further change to different functionalities. TMSCN is commonly used as a cyanide source that is safe and easy to handle when compared to HCN and metal cyanides as NaCN or KCN [5].

Many reports on C—C bond formation by cyanosilylation reactions using both homogeneous [6] and heterogeneous catalysis are available [7]. Chiral homogeneous systems, based on well established procedures using chiral organometallic and organocatalytic systems have been described [8]. The activation of TMSCN may be promoted by a wide range of nucleophiles, such as amines, phosphines, phosphazanes and alkaline earth metal oxides. On the other hand, Lewis acid catalysts have been widely investigated because they can act as electrophilic catalyst for the activation of carbonyl compounds. Examples of this type of cyanosilylation reactions were performed with simple metal salts as catalysts, viz. $Yb(OTf)_3$ [9], $Yb(CN)_3$ [10], $Cu(OTf)_2$ [11], ZnI_2 [12], KCN:18-crown-6 [13], LiCl and $LiClO_4$ [14], R_2SnCl_2 an Sn-montmorillonite [15], $MgBr_2.Et_2O$ [16], $Zr(KPO_4)_2$ [17], $VO(OTf)_2$ [18], $FeCl_3$ [19], $InBr_3$ [20], NbF_5 [21] and $Fe(Cp)_2PF_6$ [22]. Other procedures using a hydrazone-based Cu(II) catalyst [23] a 3-aminopyrazine-2-carboxylate based Pb(II) catalyst [24], a flexible tricarboxylate Gd(II) coordination polymer [25] and a 3,3′,5,5′-azobenzentetracarboxylic acid based Mg(II) catalyst [26] have also been described.

Curiously, for ruthenium, which is well-known for its unique catalytic behaviour, only very few reports have come out in the literature (Scheme 1) [27]. Ohkuma and co-workers described the synthesis of cyanosilyls from TMSCN and carbonyl compounds (aldehydes

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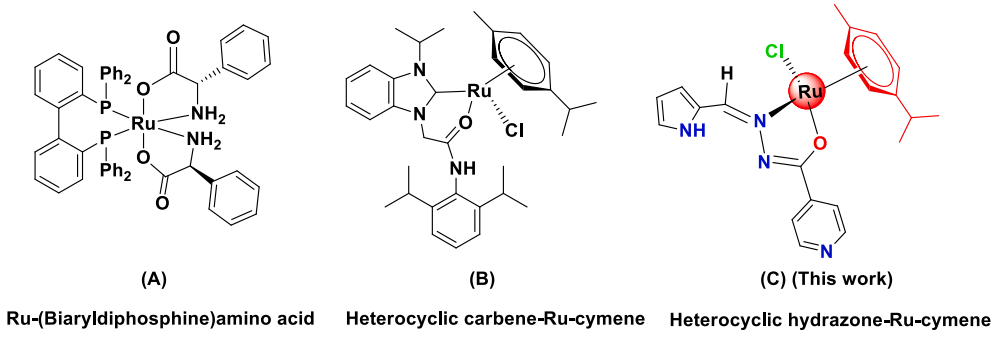


Scheme 1. Ruthenium(II) catalysts for the synthesis of cyanosilylethers.

[27(a,b)], keto esters [27c], α,α-dialkoxy ketones, β,β-dialkoxy ketones, α-alkoxy, α-amino and alkynyl ketones [27(d,e)]) using biaryl diphosphine Ru(II) aminoacids as catalysts (**A**) and, more recently, Ghosh *et al.* reported a class of cationic ruthenium(II) arene complexes displaying O-functionalized *N*-heterocyclic carbenes that act as catalysts for cyanosilylation reactions at room temperature, under solvent-free conditions (**B**) [27f].

Taking in account that catalysts with heterocyclic moieties display, in general, better activity than those having simple aryl groups, we prepared complexes with two different heterocyclic fragments (**C**). Here we report new half-sandwich ruthenium(II) complexes with heterocyclic hydrazone ligands and its behaviour as catalyst for the cyanosilylation of a wide range of carbonyl compounds, at room temperature, with excellent yields.

2. Experimental section

2.1. General considerations

The elemental analyses of the compounds were accomplished using an analytical function testing Vario EL CHN analyser. The melting points of the compounds were valued with the guide of Boetius microheating label. Bruker 783 FT-IR spectrometer was used for recording IR spectra. The absorption spectra of the ligands and complexes were measured on a Cary 300 Bio UV–Vis Varian spectrophotometer from the solutions of chloroform, 10^{-3} M, in quartz cuvettes (1 cm optical path) in the range of 800–200 nm. NMR spectra of the compounds were carried out using a Bruker Advances III HD Nanobay 400 MHz and Bruker (Avance) 300 MHz FT- NMR spectrometer at 295 K, referenced internally to residual proton-solvent (^{1}H) or solvent (^{13}C) resonances, and reported in parts per million (ppm) related to tetramethylsilane (0 ppm). The ESI-MS spectral analysis was performed in positive mode on a Q-TOF-Mass Spectrometer.

Commercially available $RuCl_3{\cdot}3H_2O$ was used as supplied from SRL Pvt. Ltd. All the solvents, reagents and the compounds pyrrole-2-carboxaldehyde, 2-furoic hydrazide, thiophene-2-carboxylic acid hydrazide and 4-pyridinecarboxylic acid hydrazide were acquired from Merck and Aldrich. The starting material $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ was prepared according to literature [28].

2.2. General method for the syntheses of pyrrole-2-carboxaldehyde hydrazone derivatives

The pyrrole-2-carboxaldehyde hydrazone precursors (**HL$^{1-3}$**) were prepared by refluxing a mixture of pyrrole-2-carboxaldehyde (1 mmol) and 2-furoic hydrazide, thiophene-2-carboxylic acid hydrazide or 4-pyridinecarboxylic acid hydrazide (1 mmol) in 15 mL of ethanol for 8 h. The solution was concentrated and the precipitate obtained was washed with cold ethanol followed by dried in vacuum.

2.2.1. Synthesis of N'-((1H-pyrrol-2-yl)methylene)furan-2-carbohydrazide (HL^1)

Yield: 76%; m.p.: 238 °C; Anal. calcd. for $C_{10}H_9N_3O_2$: C, 59.11; H, 4.46; N, 20.68. Found: C, 59.07; H, 4.44; N, 20.65. FT-IR: pyrrole –NH, 3199 cm^{-1}; NH, 3113 cm^{-1}; C═N, 1641 cm^{-1}; C═O, 1563 cm^{-1}. UV–Vis (DMSO, λ_{max} [nm] (10^{-3} ε [M^{-1} cm^{-1}])): 382 (1157), 284 (2188). ^{1}H NMR (400 MHz, DMSO-d_6) (δ ppm): 11.56 (s, 1H, –N*H*), 11.33 (s, 1H, pyrrole –N*H*), 8.29 (s, 1H, *H*C = N), 7.91–6.14 (overlapping, 6H total, Ar*H*). ^{13}C NMR (100 MHz, DMSO-d_6) (δ ppm): 154.3 (*C*═O), 141.4 (H*C* = N), 147.4, 145.9, 127.5, 123.1, 114.8, 114.0, 112.5, 109.8 (H*C* = N, $Ar_{Pyrrole}$ and Ar_{Furane}). ESI-MS: *m/z* = 203.07 [M + H]$^+$.

2.2.2. Synthesis of N'-((1H-pyrrol-2-yl)methylene)thiophene-2-carbohydrazide (HL^2)

Yield: 80%; m.p.: 249 °C; Anal. calcd. for $C_{10}H_9N_3OS$: C, 54.78; H, 4.14; N, 19.16. Found: C, 54.72; H, 4.13; N, 19.12. FT-IR: pyrrole –NH, 3248 cm^{-1}; NH, 3187 cm^{-1}; C═N, 1592 cm^{-1}; C═O, 1557 cm^{-1}. UV–Vis (DMSO, λ_{max} [nm] (10^{-3} ε [M^{-1} cm^{-1}])): 391 (1157), 292 (2294). ^{1}H NMR (400 MHz, DMSO-d_6) (δ ppm): 11.57 (s, 1H, –N*H*), 11.19 (s, 1H, pyrrole –N*H*), 8.15 (s, 1H, *H*C = N), 7.98–6.15 (overlapping, 6H total, Ar*H*). ^{13}C NMR (100 MHz, DMSO-d_6) (δ ppm): 157.8 (*C*═O), 141.2 (H*C* = N), 139.1, 131.8, 128.9, 128.5, 127.4, 123.1, 114.0, 109.8 (H*C* = N, $Ar_{Pyrrole}$ and $Ar_{Thiophene}$). ESI-MS: *m/z* = 219.05 [M + H]$^+$.

2.2.3. Synthesis of N'-((1H-pyrrol-2-yl)methylene)isonicotinohydrazide (HL^3)

Yield: 87%; m.p.: 215 °C; Anal. calcd. for $C_{11}H_{10}N_4O$: C, 61.67; H, 4.71; N, 26.15. Found: C, 61.64; H, 4.69; N, 26.11. FT-IR: pyrrole –NH, 3268 cm^{-1}; NH, 3200 cm^{-1}; C═N, 1693 cm^{-1}; C═O, 1595 cm^{-1}. UV–Vis (DMSO, λ_{max} [nm] (10^{-3} ε [M^{-1} cm^{-1}])): 389 (1053), 288 (2379). ^{1}H NMR (400 MHz, DMSO-d_6) (δ ppm): 11.76 (s, 1H, –N*H*), 11.61 (s, 1H, pyrrole –N*H*), 8.77 (s, 1H, *H*C = N), 8.30–6.12 (overlapping, 7H total, Ar*H*). ^{13}C NMR (100 MHz, DMSO-d_6) (δ ppm): 161.5 (*C*═O), 141.4 (H*C* = N), 150.7, 142.4, 138.7, 127.2, 123.4, 122.0, 114.4, 113.4, 109.9 (H*C* = N, $Ar_{Pyrrole}$ and $Ar_{Pyridine}$). ESI-MS: *m/z* = 214.09 [M + H]$^+$.

2.3. Syntheses of Half-Sandwich (η^6-p-cymene) Ruthenium(II) complexes (1–3)

One equivalent of $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ was added to a dichloromethane solution (15 mL) containing two equivalents of the pyrrole-2-carboxaldehyde hydrazone derivatives (**HL$^{1-3}$**) and few drops of triethylamine were added. The reaction mixture was stirred at room temperature for 5 h. A gradual colour change from reddish orange to brown was observed. The complexes were crystallized from CH_2Cl_2 /hexane solutions.

2.3.1. Synthesis of [Ru(η^6-p-cymene)(Cl)(L^1)] (1)

Yield: 79%; m.p. : 131 °C; Anal. calcd. for $C_{20}H_{22}N_3O_2ClRu$: C, 50.79; H, 4.69; N, 8.89. Found: C, 50.73; H, 4.67; N, 8.85. FT-IR: NH, 3281 cm^{-1}; C═N, 1605 cm^{-1}; C—O, 1227 cm^{-1}. UV–Vis ($CHCl_3$, λ_{max} [nm] (10^{-3} ε [M^{-1} cm^{-1}]): 369 (1190), 298 (6753), 252 (7845). ^1H NMR (300 MHz, $CDCl_3$) (δ ppm): 11.02 (s, 1H, pyrrole N—*H*), 8.78 (s, 1H, *H*C = N), 7.44–6.39 (overlapping, 6H total, Ar*H*), 5.39 (d, 1H, *p*-cym Ar*H*), 5.28 (d, 1H, *p*-cym Ar*H*), 5.00 (d, 1H, *p*-cym Ar*H*), 4.71 (d, 1H, *p*-cym Ar*H*), 2.62 (sept, 1H, *p*-cym ArC*H*(CH_3)$_2$), 2.24 (s, 3H, *p*-cym Ar(C*H*$_3$)), 1.29 (d, 3H, *p*-cym ArCH(C*H*$_3$)$_2$), 1.18 (d, 3H, *p*-cym ArCH(C*H*$_3$)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$) (δ ppm): 154.3 (*C*═O), 141.4 (H*C* = N), 147.4, 145.9, 127.5, 123.1, 114.8, 114.0, 112.5, 109.8, (H*C* = N, $Ar_{Pyrrole}$ and Ar_{Furane}), 101.01, 98.08 (*p*-cym C_qAr), 86.27, 84.92, 82.18, 79.04 (*p*-cym C_HAr), 22.78, 19.01 (*p*-cym Ar*C*H(CH_3)$_2$ and Ar(*C*H$_3$)), 8.40, 7.44 (*p*-cym ArCH(*C*H$_3$)$_2$). ESI-MS: *m/z* = 473.04 $[M-Cl]^+$.

2.3.2. Synthesis of [Ru(η^6-p-cymene)(Cl)(L^2)] (2)

Yield: 84%; m.p.: 208 °C; Anal. calcd. for $C_{20}H_{22}N_3OSClRu$: C, 49.12; H, 4.53; N, 8.59. Found: C, 49.09; H, 4.50; N, 8.53. FT-IR: NH, 3252 cm^{-1}; C═N, 1600 cm^{-1}; C—O, 1230 cm^{-1}. UV–Vis ($CHCl_3$, λ_{max} [nm] (10^{-3} ε [M^{-1} cm^{-1}]): 371 (4456), 300 (3035), 262 (4070). ^1H NMR (300 MHz, $CDCl_3$) (δ ppm): 11.58 (s, 1H, pyrrole N—*H*), 8.93 (s, 1H, *H*C = N), 7.90–6.28 (overlapping, 6H total, Ar*H*), 5.58 (d, 1H, *p*-cym Ar*H*), 5.43 (d, 1H, *p*-cym Ar*H*), 5.22 (d, 1H, *p*-cym Ar*H*), 5.00 (d, 1H, *p*-cym Ar*H*), 2.28 (sept, 1H, *p*-cym ArC*H*(CH_3)$_2$), 2.16 (s, 3H, *p*-cym Ar(C*H*$_3$)), 1.41 (d, 3H, *p*-cym ArCH(C*H*$_3$)$_2$), 1.22 (d, 3H, *p*-cym ArCH(C*H*$_3$)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$) (δ ppm): 168.7 (*C*═O), 141.8 (H*C* = N), 159.2, 148.9, 147.8, 145.7, 139.8, 128.5, 127.4, 121.2 (H*C* = N, $Ar_{Pyrrole}$ and $Ar_{Thiophene}$), 101.2, 98.7 (*p*-cym C_qAr), 92.5, 89.5, 85.6, 82.9 (*p*-cym C_HAr), 22.8, 19.5 (*p*-cym Ar*C*H(CH_3)$_2$ and Ar(*C*H$_3$)), 11.1, 8.8 (*p*-cym ArCH(*C*H$_3$)$_2$). ESI-MS: *m/z* = 489.02 $[M-Cl]^+$.

2.3.3. Synthesis of [Ru(η^6-p-cymene)(Cl)(L^3)] (3)

Yield: 89%; m.p.: 178 °C; Anal. calcd. for $C_{21}H_{23}N_4OClRu$: C, 52.12; H, 4.79; N, 11.58. Found: C, 52.08; H, 4.76; N, 11.51. FT-IR: NH, 3239 cm^{-1}; C═N, 1663 cm^{-1}; C—O, 1240 cm^{-1}. UV–Vis ($CHCl_3$, λ_{max} [nm] (10^{-3} ε [M^{-1} cm^{-1}]): 377 (2663), 279 (1831), 248 (1737). ^1H NMR (300 MHz, $CDCl_3$) (δ ppm): 11.03 (s, 1H, pyrrole N—*H*), 8.78 (s, 1H, *H*C = N), 8.63–6.41 (overlapping, 7H total, Ar*H*), 5.43 (d, 1H, *p*-cym Ar*H*), 5.31 (d, 1H, *p*-cym Ar*H*), 5.04 (d, 1H, *p*-cym Ar*H*), 4.70 (d, 1H, *p*-cym Ar*H*), 2.60 (sept, 1H, *p*-cym ArC*H*(CH_3)$_2$), 2.24 (s, 3H, *p*-cym Ar(C*H*$_3$)), 1.19 (d, 3H, *p*-cym ArCH(C*H*$_3$)$_2$), 1.17 (d, 3H, *p*-cym ArCH(C*H*$_3$)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$) (δ ppm): 171.4 (*C*═O), 145.4 (H*C* = N), 151.9, 149.8, 139.5, 132.2, 125.8, 123.0, 122.4, 117.5, 111.3 (H*C* = N, $Ar_{Pyrrole}$ and $Ar_{Pyridine}$), 102.6, 100.5 (*p*-cym C_qAr), 92.6, 84.4, 81.7, 81.2 (*p*-cym C_HAr), 22.2, 18.5 (*p*-cym Ar*C*H(CH_3)$_2$ and Ar(*C*H$_3$)), 12.0, 8.6 (*p*-cym ArCH(*C*H$_3$)$_2$). ESI-MS: *m/z* = 484.06 $[M-Cl]^+$.

2.4. General procedure for the synthesis of cyanosilylethers

Catalyst **3** (0.5 mol%) was added to a mixture of aldehyde (1 mmol) with TMSCN (1.5 mmol) and diethyl ether (3 mL). The reaction mixture was stirred at room temperature for 6 h and the reaction was monitored by TLC. After the completion of the reaction, the solvent was evaporated under vacuum. The analysis of the products was performed by proton NMR spectra and the isolated yield was calculated.

2.5. General procedure for X-ray crystallography

Crystallographic and experimental details of data collection and crystal structure determinations for the compounds are available in Table 1. Suitable crystals of compounds **1–3** were coated and selected in Fomblin® oil. Data were collected using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) on a Bruker AXS-KAPPA APEX II diffractometer. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT on all observed reflections [29]. Absorption corrections were applied using SADABS [30]. The structures were solved by direct methods using SIR2004 [31]. Structure refinement was done using SHELXL [32], included in the WINGX-Version 1.80.01 system of programs [33]. Hydrogen atoms were inserted in calculated positions and allowed to refine in the parent atoms. Torsion angles, mean square planes and other geometrical parameters were calculated using SHELX [32]. Illustrations of the molecular structures were made with ORTEP-3 for Windows [34]. Data for structures **1–3** were deposited in CCDC under the deposit numbers 1966389, 1,966,390 and 1966391, respectively, and can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

3. Results and discussion

The ligand precursors and the ruthenium complexes described are presented in Schemes 2 and 3, respectively. Pyrrole-2-carboxaldehyde hydrazones (**HL$^{1-3}$**) were synthesized with excellent yields by a simple and direct method that consists in the 1:1 reaction of aldehydes with 2-carboxylic acid hydrazine derivatives. Treatment of [Ru(η^6-*p*-cymene)(Cl)$_2$]$_2$ with **HL^i** (i = 1–3) in a 1:2 M ratio led to the formation of complexes of general formula [Ru(η^6-*p*-cymene)(Cl)(L^i)] (**1–3**) in high yields.

The IR spectral data of the ligand precursors show absorptions in the regions 3268–3199 cm^{-1}, 3200–3113 cm^{-1}, 1693–1592 cm^{-1} and 1595–1557 cm^{-1} that are assigned to $\nu_{pyrrole\text{-}NH}$, $\nu_{hydrazide\text{-}N\text{-}H}$, $\nu_{C=N}$ and $\nu_{C=O}$, respectively. In the IR spectra of the complexes the bands due to hydrazone $\nu_{N\text{-}H}$ and carbonyl $\nu_{C=O}$ groups are not present due to the coordination of ruthenium in the imidolate enolate form. New bands due to the coordination of azomethine nitrogen and imidolate oxygen to the ruthenium come up at 1663–1605 cm^{-1} and 1240–1227 cm^{-1} respectively [35].

Pyrrole-2-carboxaldehyde hydrazone precursors (**HL$^{1-3}$**) display absorption bands at 292–288 nm and 391–382 nm, assigned to the π-π* and n-π* transitions. The latter transitions are particularly intense in the spectra of the complexes at 262–248 nm and 300–279 nm. Moreover, the spectra of the complexes also reveal low intense bands in the range 377–369 nm that are assigned to Ru(dπ)-to-(Lπ*) (MLCT) transitions [36].

The ^1H NMR spectra of the ligands (**HL$^{1-3}$**) show three singlets at δ 11.76–11.56 ppm, δ 11.61–11.19 ppm and δ 8.77–8.26 ppm that correspond to hydrazide-N*H*, pyrrole-N*H* and imine *H*C = N protons respectively. The aromatic protons appear at δ 8.30–6.12 ppm.

The solid-state molecular structures of complexes **1–3** were determined by single crystal X-ray diffraction. Compounds **2** and **3** crystalize in the monoclinic $P2_1/c$ space group while **1** crystalizes in the triclinic *P*-1 space group. ORTEP depictions of the molecular structures of **1–3** are displayed in Figs. 1–3, respectively, and relevant distances and angles are shown in Table 2.

All complexes display a typical three-legged piano-stool geometry with distances between ruthenium and the ring centroids (Ru-Ph_{CT}) ranging from 1.666(2) to 1.682(2) Å. The distances between the metal centre and the chloride and the bidentate ligands are within the usual ranges observed for this type of bonds [37]. In general, the structural parameters obtained for **1–3** agree with those reported for other [Ru(η^6-*p*-cymene)(Cl)(L)] complexes [38]. Hydrogen bonds are established between Cl(1) and the hydrogen atoms H(3 N) and H(4 N) of the pyrrole rings in complexes **1–3** with distances between of 2.32(3) and 2.58(4) Å (see Table 3 for details) [39].

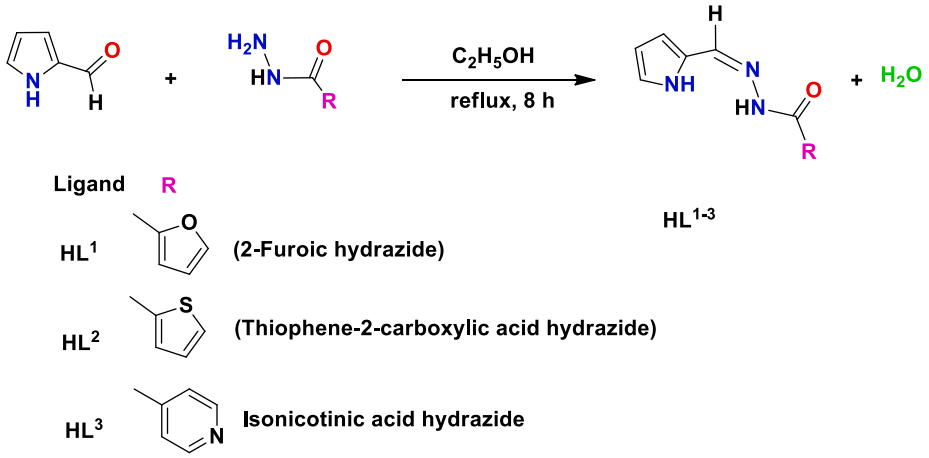
3.1. Catalytic studies for the synthesis of Cyanosilylether derivatives

The ruthenium complexes (**1–3**) were successfully used as catalysts

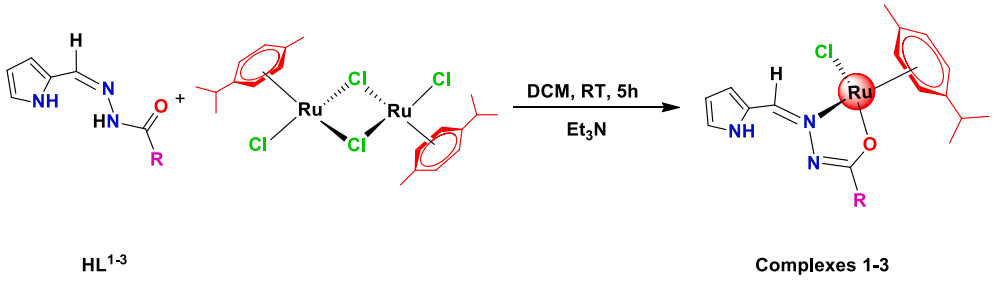
Table 1
Crystal data and structure refinement for compounds **1–3**.

	1	2	3
Empirical formula	$C_{20}H_{22}ClN_3O_2Ru$	$C_{20}H_{22}ClN_3ORuS$	$C_{21}H_{23}ClN_4ORu$
Formula weight	472.93	488.99	483.95
Temperature (K)	298(2)	150(2)	150(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P*-1	$P2_1/c$	$P2_1/c$
Unit Cell Dimensions:			
a (Å)	7.798(3)	10.8300(4)	10.9087(3)
b (Å)	10.710(4)	12.5858(5)	7.6484(2)
c (Å)	12.566(5)	15.0455(5)	23.3743(7)
α (°)	111.31(1)	90	90
β (°)	100.47(2)	99.294(2)	93.380(1)
γ (°)	92.45(2)	90	90
Volume ($Å^3$)	954.6(6)	2023.8(1)	1946.82(9)
Z	2	4	4
Calculated density (g m^{-3})	1.645	1.605	1.651
Absorption coefficient (mm^{-1})	0.982	1.025	0.963
F (000)	480	992	984
Crystal size (mm)	0.30 × 0.30 × 0.10	0.26 × 0.28 × 0.30	0.26 × 0.28 × 0.30
Theta range for data collection (°)	2.056 – 26.450	3.186 – 25.675	3.255 – 31.611
Limiting indices	$-9 \le h \le 9$, $-13 \le k \le 13$, $-15 \le l \le 15$	$-13 \le h \le 13$, $-15 \le k \le 14$, $-18 \le l \le 18$	$-16 \le h \le 16$, $-11 \le k \le 9$, $-28 \le l \le 34$
Reflections collected/unique [R_{int}]	26647/3897 [0.0605]	30996/3838 [0.0584]	22779/6518[0.0509]
Completeness to θ (%)	99.4 (θ = 25.242)	99.8 (θ = 25.242)	99.8 (θ = 25.242)
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data/restraints/parameters	3897/0/251	3838/12/270	6518/0/260
Goodness-of-fit on F^2	1.211	1.042	1.071
Final *R* indices [$I > 2\sigma(I)$][1]	R_1 = 0.0309, wR_2 = 0.0665	R_1 = 0.0256, wR_2 = 0.0631	R_1 = 0.0308, wR_2 = 0.0736
R indices (all data)[1]	R_1 = 0.0368, wR_2 = 0.0685	R_1 = 0.0293, wR_2 = 0.0650	R_1 = 0.0381, wR_2 = 0.0764
Absorption correction	Multi-scan	Multi-scan	Multi-scan
Largest diff. peak/hole (e $Å^{-3}$)	0.570 and −0.525	0.675 and −0.567	0.652 and −0.488

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



Scheme 2. Pyrrole-2-carboxaldehyde hydrazone derivatives (**HL^{1-3}**).



Scheme 3. Synthesis of ruthenium(II) (*p*-cymene) complexes (**1–3**).

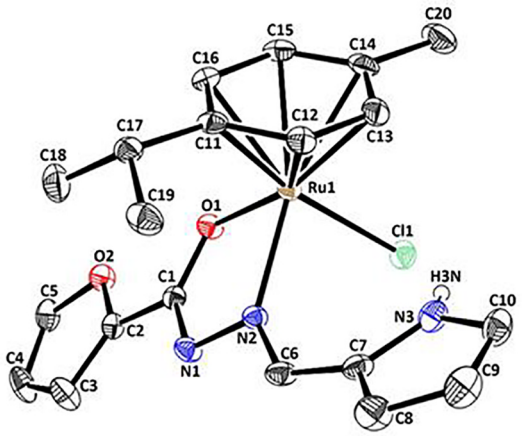


Fig. 1. ORTEP diagram of **1** with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted for clarity.

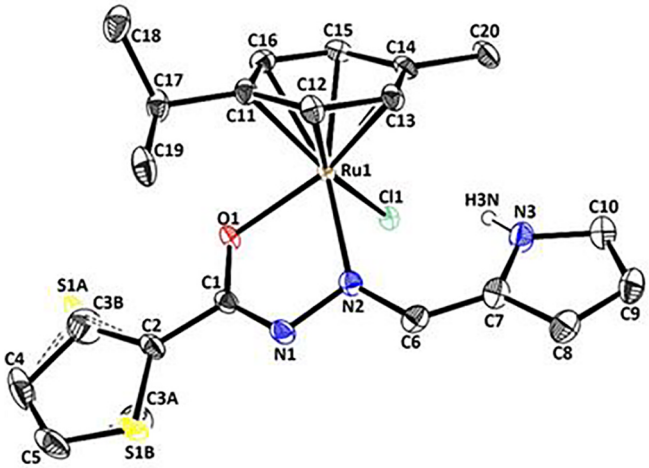


Fig. 2. ORTEP diagram of **2** with thermal ellipsoids at 40% probability level. Selected hydrogen atoms are omitted for clarity.

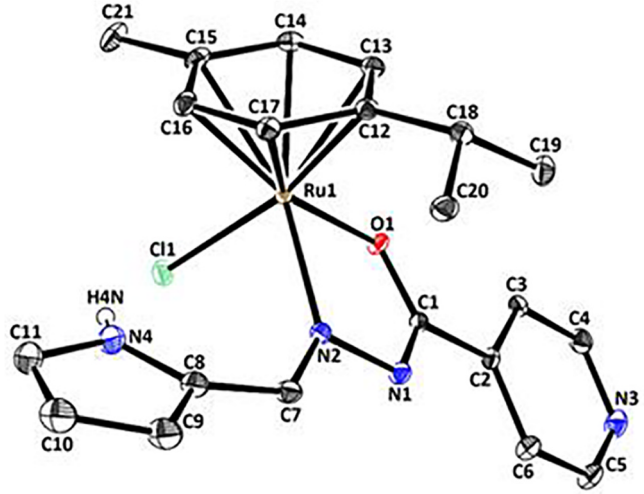


Fig. 3. ORTEP diagram of **3** with thermal ellipsoids at 40% probability level. Selected hydrogen atoms are omitted for clarity.

for the cyanosilylation of aryl, heteroaryl and aliphatic aldehydes with trimethylsilyl cyanide (TMSCN) at room temperature. The catalytic reactions were optimized using benzaldehyde and TMSCN as substrates varying the solvents with 1 mol% of Ru-catalyst **3**.

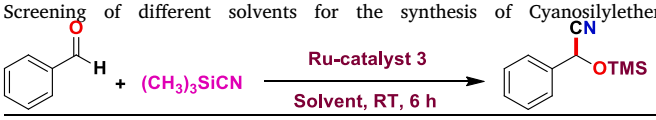
Table 2
Hydrogen bond distances (Å) and angles (°) in compounds 1, 2 and 3.

	D-H…A	d(D-H)	d(H…A)	d(D…A)	(DĤA)
1	N(3)-H(3 N)···Cl(1)	0.86(4)	2.58(4)	3.382(3)	156(3)
2	N(3)-H(3 N)···Cl(1)	0.94(3)	2.32(3)	3.207(2)	157(3)
3	N(4)-H(4 N)···Cl(1)	0.83(2)	2.47(2)	3.244(2)	155(2)

Table 3
Selected distances (Å) and angles (°) of compounds 1–3.

	Ru-N	**Ru-Cl**	**Ru-O**	**Ru-[C_6Plane]**
1	2.089(2)	2.421(1)	2.069(2)	1.682(2)
2	2.095(2)	2.4078(6)	2.066(2)	1.666(1)
3	2.084(1)	2.4107(5)	2.069(1)	1.6717(7)
	Cl-Ru-N	***N*-Ru-O**	**O-Ru-Cl**	
1	85.27(7)	76.22(9)	87.67(6)	
2	86.27(6)	76.07(7)	88.50(5)	
3	86.05(4)	76.14(5)	87.42(4)	

Table 4
Screening of different solvents for the synthesis of Cyanosilylether.[a]



Entry	**Solvent**	**Yield[b] (%)**
1	Benzene	73
2	Chloroform	58
3	Dichloromethane	93
4	Toluene	69
5	THF	90
6	Diethyl ether	97
7	DMSO	34
8	Acetone	86
9	Acetonitrile	72
10	DMF	48
11	Methanol	63

[a] Conditions: Benzaldehyde (1 mmol), TMSCN (1.5 mmol), catalyst **3** (1 mol %) in the presence of solvent (3 mL), room temperature for 6 h. **[b]** Isolated yield.

We have screened the reaction by using various solvents. The polar solvents such as DMSO, DMF, methanol, acetonitrile and acetone (entries 7, 10, 11, 9 & 8 respectively) led to moderate to high conversions in the range 34–86%. The non-polar solvents benzene and toluene (entries 1 & 4) led to moderate conversions of 73 & 69%. But, the borderline polar solvents with low boiling point such as THF, DCM and diethylether (entries 5, 3 & 6 respectively) led to excellent conversions in the range 90–97%. Hence, the best solvent to perform the cyanosilylation reaction is diethylether. Further, the results are summarized in Table 4.

The most effective catalyst was determined (See Table 5) in diethyl ether using the experimental conditions that were used for the choice of the solvent. The performance of the catalysts (1, 2 and 3) are in the following order 1 < 2 < 3, (ie., 88, 93 & 97% respectively). It is clear

Table 5
Screening of catalyst on Cyanosilylation reaction.[a]

Entry	**Catalyst**	**Yield[b] (%)**
1	[Ru(*p*-cymene)(Cl)(L^1)] **(1)**	88
2	[Ru(*p*-cymene)(Cl)(L^2)] **(2)**	93
3	[Ru(*p*-cymene)(Cl)(L^3)] **(3)**	97

[a] Conditions: Benzaldehyde (1 mmol), TMSCN (1.5 mmol), catalyst **1–3** (1 mol%) in the presence of Et_2O (3 mL), room temperature for 6 h. **[b]** Isolated yield.

Table 6
Effect of catalyst loading.[a]

Entry	Mol % of catalyst	Yield[b] (%)
1[c]	–	–
2	2.5	79
3	2.0	88
4	1.5	90
5	1.0	94
6	0.5	99
7	0.3	73
8	0.1	65

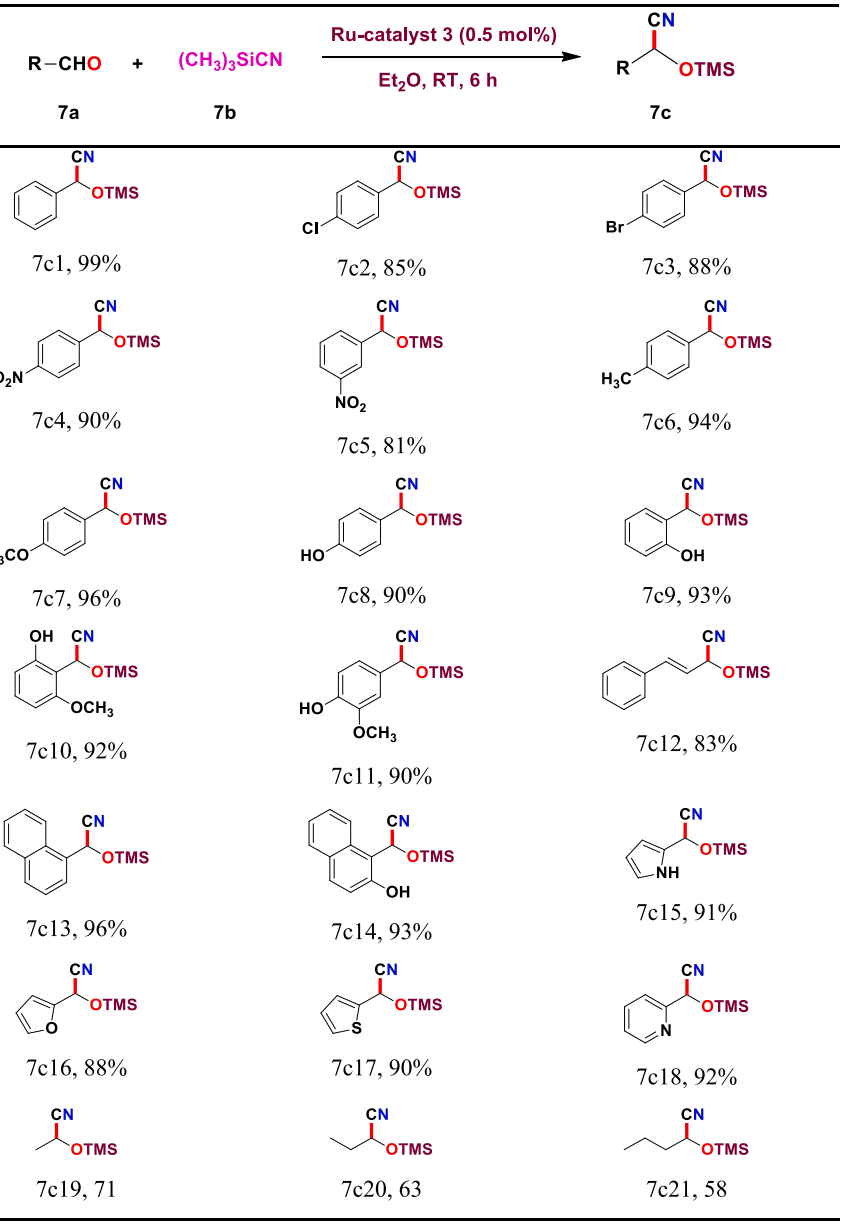
[a] Conditions: Benzaldehyde (1 mmol), TMSCN (1.5 mmol), catalyst **3** (2.5–0.1 mol%) in the presence of Et_2O (3 mL), room temperature for 6 h. **[b]** Isolated yield. **[c]** Absence of catalyst.

that the variation in the reactivity of the catalysts (1, 2 & 3) is due to the change in their ligand moiety (furan, thiophene & pyridine respectively). However, the difference in their performance is only marginal. It reveals the week influence of the substituents on their performance. Hence, it is hard to specify the reason for the slightly better performance of the catalyst **3** over other two catalysts.

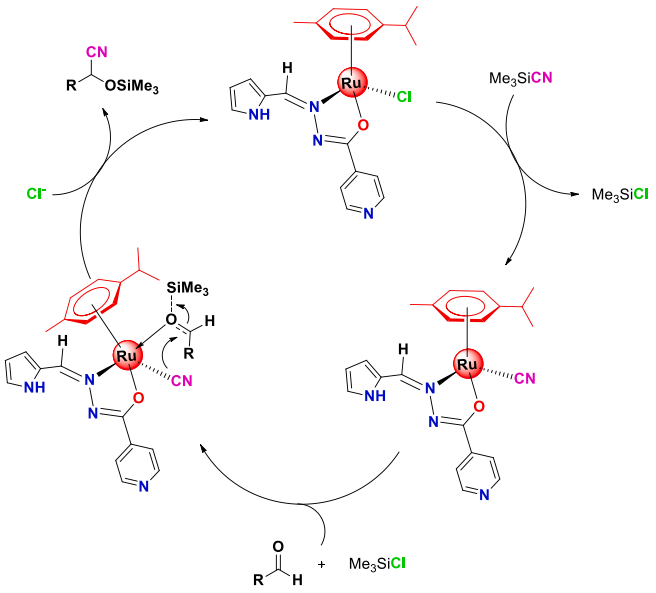
The effect of catalyst loading was performed by varying the concentration of catalyst **3** from 2.5 to 0.1 mol%. For this optimization reaction, we have followed the same reaction conditions and substrates in diethyl ether. The results are given in the Table 6. It reveals 0.5 mol% of the catalyst is best suited for this cyanosilylation reaction.

Using the optimal reaction conditions, Et_2O and 0.5 mol% of catalyst **3**, we have carried out the synthesis of several cyanosilylethers in good to excellent yields using a wide variety of aldehydes viz., aryl, fused ring aryl, aryl with extended conjugated double bond, heterocyclic and aliphatic aldehydes. The results are shown in Table 7 and

Table 7
Ruthenium catalysed Cyanosilylether synthesis: Scope of aldehyde substrates[a].



[a] Conditions: Aldehydes (1 mmol), TMSCN (1.5 mmol), catalyst **3** (0.5 mol%) in the presence of Et_2O (3 mL), room temperature for 6 h. **[b]** Isolated yield.



Scheme 4. Plausible mechanism for silylcyanation of aldehydes.

allow the following remarks: i) benzaldehyde afforded corresponding trimethylsilyl cyanide with 99% yield (entry 7c1); ii) the catalyst gives good to excellent yield for all the kinds of substrates except aliphatic aldehydes (entries 7c19-7c21, 71–58%); iii) electron donor groups in *ortho-, meta-* and *para-* positions (entries 7c6-7c11, 96–90%) give slightly better yields than the ones obtained with electron accepting substituents (entries 7c2-7c5, 90–81%), a difference that may be related with the higher nucleophilicity of the first group of substrates; iv) the catalyst is also well suited for substrates having extended conjugated double bonds (7c12, 83% yield), fused aryl rings (7c13, 7c14, 96% yield) and heterocyclic substrates (7c15-7c18, 88–92% yields).

Scheme 4 depicts a possible mechanism for the reactions. The first step of the reaction should involve the replacement of the chloride by the cyanide ligand in the coordination sphere of ruthenium leading to the formation of a new Ru-CN bond and to the generation of TMSCl. The subsequent interaction of the aldehyde with the ruthenium and TMSCl is expected to increase the electrophilicity of the carbonyl carbon favouring the nucleophilic attack of the cyanide, leading to the formation of the products.

4. Concluding remarks

In this manuscript we report the synthesis, characterization and molecular structures of new half-sandwich ruthenium(II) (*p*-cymene) complexes with heterocyclic hydrazone ligands and evaluate their ability as catalysts in cyanosilylation of aldehydes with TMSCN. The procedure uses a readily prepared and easy to handle catalyst that does not require any additional base and allows the isolation of the products by a simple workup. Our catalyst is well suited for a diverse range substrates having broad functional group compatibility and substrate scope (aryl, heteroaryl, aryl with fused ring, aryl with conjugated double bond and aliphatic aldehydes), leading to good to excellent yields.

CRediT authorship contribution statement

Govindasamy Vinoth: Conceptualization, Methodology, Writing - original draft. **Sekar Indira:** Visualization, Spectral discussion. **Madheswaran Bharathi:** Visualization, Spectral discussion. **Luis G. Alves:** XRD structure solving & writing. **Ana M. Martins:** XRD structure solving & writing. **Kuppannan Shanmuga Bharathi:** Conceptualization, Validation, Methodology, Supervision, review & editing.

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2020.120006.

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