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Bis(phenoxy-imine) ruthenium(II) carbonyl complexes: syntheses, structures and their catalytic activities for conversion of aldehydes to nitriles

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ABSTRACT

Three new ruthenium(II) carbonyl complexes that bear phenoxyimine chelate ligands, $[RN = CH(C_6H_4O)]_2Ru(CO)_2$ (1: $R = 2,6-Me_2C_6H_3$; **2**: $R = 4-OMeC_6H_4$; **3**: $R = 4-ClC_6H_4$) have been synthesized. These mononuclear ruthenium(II) complexes were fully characterized by elemental analysis, FT–IR, and ¹H and ¹³C NMR. Furthermore, the molecular structures of **1-3** were determined by X-ray crystal diffraction analysis. In the presence of NaHCO₃ as the base, the Ru carbonyl complexes showed moderate to good catalytic activities for the conversion of aldehydes to nitriles *via* the dehydration of aldoximes.

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KEYWORDS

Phenoxy-imine ligands; ruthenium carbonyl complexes; nitriles; dehydration; catalytic conversion



1. Introduction

Nitriles are one of the most important class of compounds that are widely used as intermediates for the synthesis of agrochemicals, pharmaceuticals and biologically active compounds [1–3]. The most well-known procedures for preparation of nitriles include the reaction of aqueous ammonia with alcohols and the dehydration of amides with the aid of dehydrating agents (such as acetonitrile, and silane) [4–8]. However, the efficiency of these common methods is limited owing to the high activation energy barrier and the formation of a large amount of waste, which is often hazardous to the environment. Thus, the development of more sustainable and efficient approaches for their production is always in demand.

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To overcome some of the above economic and environmental related problems, the synthetic method of direct conversion of primary amines to nitriles via dehydrogenation has received increased attention [9-11]. In 2016, Szymczak and co-workers reported the synthesis of nitriles through acceptorless dehydrogenation of amines catalyzed by an N,N,N-pincer ruthenium(II) complex [12]. Analogously, the aerobic oxidative dehydrogenative reaction of primary amines to nitriles using Ru^{II}/TEMPO/O₂ catalytic system has also been developed [13]. But, these reactions are usually carried out at high temperature (\sim 130 °C) and long reaction times (\sim 24 h) were also needed. Another alternative approach for the synthesis of nitriles is dehydration of aldoximes [14, 15]; the dehydration of aldoximes generated in situ from aldehydes and hydroxylamine hydrochloride is an efficient protocol [16, 17], which can eliminate the pre-preparation of aldoximes and the formation of water as the only by-product. For example, Enthaler et al. reported the zinc-catalyzed conversion of aldehydes and hydroxylamine hydrochloride to nitriles with high activity [18], and a variety of substituted benzaldehyde molecules could be converted to their corresponding nitriles in good to excellent yields. The straightforward dehydration of aldoximes to the nitriles is still rare since the rearrangement of aldoximes into primary amides also occurs during the reaction [19, 20]. Hence, investigation of the synthesis of nitriles via dehydration of aldoximes catalyzed by new transition metal catalysts is highly desired.

Recently, transition metal carbonyl complexes, especially ruthenium carbonyl complexes, have attracted much attention because of their vital applications in the preparation of nitriles [13, 21]. Nagashima and co-workers reported an acenaphthene-based triruthenium carbonyl cluster for dehydration of primary carboxamides to nitriles using hydrosilane as dehydrating agent [22]. More recently, we utilized N,O-bidentate ligand-supported trinuclear ruthenium carbonyl complexes to catalyze aerobic oxidation of primary benzylic amines to amides and nitriles with high activity and selectivity [23]. However, the reactions catalyzed by mononuclear Ru carbonyl complexes and the conversion of aldehydes to nitriles occurring through dehydration of aldoximes are still rare. Herein, we report the synthesis and characterization of mononuclear ruthenium(II) carbonyl complexes containing phenoxy-imine ligands. Furthermore, these Ru complexes have been employed as catalysts for catalytic synthesis of nitriles *via* the reaction of aldehydes with hydroxylamine hydrochloride.

2. Experimental

2.1. General considerations

All manipulations were carried out using standard high-vacuum-line techniques. Solvents were distilled from appropriate drying agents under N_2 before use. Hydroxylamine hydrochloride, aniline and its derivatives were purchased from Boka Chemical Co. Other reagents were purchased from Aldrich and used without purification. ¹H- and ¹³C-NMR spectra were recorded on a Bruker AV III-500 instrument in CDCl₃ and the chemical shifts are referenced to the residual protio impurity of the deuterated solvent. IR spectra were recorded as KBr disks on a Thermo Fisher iS50 spectrometer. Elemental analyses were performed with a VarioEL III analyzer. Phenoxy-

imine ligands $RN = CHC_6H_4OH$ (**L1H**: $R = 2,6-Me_2C_6H_3$; **L2H**: $R = 4-OMeC_6H_4$; **L3H**: $R = 4-CIC_6H_4$) were synthesized according to the literature methods [24, 25].

2.2. Synthesis of bis((E)-2-(((2,6dimethylphenyl)imino)methyl)phenoxy)dicarbonyl ruthenium(II) Ru(κ²-N,O-L1)₂(CO)₂ (1)

A solution of 2,6-Me₂C₆H₃N = CHC₆H₄OH **L1H** (0.53 g, 2.35 mmol) and Ru₃(CO)₁₂ (0.30 g, 0.47 mmol) in 20 mL of toluene was heated at reflux for 8 h under an argon atmosphere. The mixture was allowed to cool to room temperature and the solvent was evaporated under vacuum. The residue was chromatographed in an Al₂O₃ column with petroleum ether and ethyl acetate as eluent to give **1** as a green powder (0.15 g, 22%). Anal. Calc. for $C_{32}H_{28}N_2O_4Ru$ (%): C, 63.5; H, 4.66; N, 4.6. Found: C, 63.4; H, 4.8; N, 4.7; ¹H NMR (CDCl₃, 500 MHz): δ 2.22 (s, 6H, CH₃), 2.69 (s, 6H, CH₃), 6.55 (t, 2H, J = 8.5 Hz, Ar-H), 6.69 (d, 2H, J = 8.5 Hz, Ar-H), 7.09-7.14 (m, 6H, Ar-H), 7.20-7.24 (m, 4H, Ar-H), 7.77 (s, 2H, N = CH); ¹³C NMR (CDCl₃, 125 MHz): δ 18.5 (CH₃), 18.9 (CH₃), 114.4 (ArC), 120.5 (ArC), 122.3 (ArC), 126.7 (ArC), 128.6 (ArC), 129.1 (ArC), 129.4 (ArC), 131.7 (ArC), 135.6 (ArC), 135.7 (ArC), 155.1 (ArC), 166.7 (ArC), 168.4 (N = CH), 197.3 (CO); IR (ν_{CO} , KBr, cm⁻¹): 2043 (s), 1970 (s).

2.3. Synthesis of bis(E)-2-(((4-methoxyphenyl)imino)methyl)phenoxy)dicarbonyl ruthenium(II) $Ru(\kappa^2-N,O-L2)_2(CO)_2$ (2)

Using a procedure similar to that described above for **1**, reaction of 4-OMeC₆H₄N = CHC₆H₄OH **L2H** (0.54 g, 2.35 mmol) and Ru₃(CO)₁₂ (0.30 g, 0.47 mmol) in 20 mL of toluene gave **2** as an orange powder (0.13 g, 18%). Anal. Calc. for C₃₀H₂₄N₂O₆Ru (%): C, 59.1; H, 3.9; N, 4.6. Found: C, 59.2; H, 3.8; N, 4.4; ¹H NMR (CDCl₃, 500 MHz): δ 3.85 (s, 6H, OCH₃), 6.59 (t, 2H, J = 7.5 Hz, Ar-H), 6.93 (d, 4H, J = 8.0 Hz, Ar-H), 7.04 (d, 2H, J = 7.5 Hz, Ar-H), 7.24 (d, 2H, J = 7.5 Hz, Ar-H), 7.36 (t, 2H, J = 7.5 Hz, Ar-H), 7.42 (d, 4H, J = 8.0 Hz, Ar-H), 8.06 (s, 2H, N = CH); ¹³C NMR (CDCl₃, 125 MHz): δ 55.5 (OCH₃), 114.0 (ArC), 115.0 (ArC), 119.9 (ArC), 122.3 (ArC), 123.8 (ArC), 135.5 (ArC), 135.8 (ArC), 152.2 (ArC), 158.3 (ArC), 166.5 (ArC), 166.9 (N = CH), 195.5 (CO); IR (υ_{CO} , KBr, cm⁻¹): 2039 (s), 1969 (s).

2.4. Synthesis of bis(E)-2-(((4-chlorophenyl)imino)methyl)phenoxy)dicarbonyl ruthenium(II) $Ru(\kappa^2-N,O-L3)_2(CO)_2$ (3)

Using a procedure similar to that described above for **1**, reaction of 4-ClC₆H₄N = CHC₆H₄OH **L3H** (0.54 g, 2.35 mmol) and Ru₃(CO)₁₂ (0.30 g, 0.47 mmol) in 20 mL of toluene gave **3** as an orange powder (0.12 g, 17%). Anal. Calc. for C₂₈H₁₈Cl₂N₂O₄Ru (%): C, 54.4; H, 2.9; N, 4.5. Found: C, 54.2; H, 2.8; N, 4.4; ¹H NMR (CDCl₃, 500 MHz): δ 6.59-6.62 (m, 2H, Ar-H), 6.95 (d, 2H, *J* = 8.5 Hz, Ar-H), 7.20 (dd, 2H, *J*₁ = 2.0 Hz, *J*₂ = 8.0 Hz, Ar-H), 7.32-7.39 (m, 10H, Ar-H), 7.98 (s, 2H, N = CH); ¹³C NMR (CDCl₃, 125 MHz): δ 115.2 (ArC), 119.5 (ArC), 122.4 (ArC), 124.2 (ArC), 129.3 (ArC), 132.8

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Complex	1	2	3
Empirical formula	C ₃₂ H ₂₈ N ₂ O ₄ Ru	C ₃₀ H ₂₄ N ₂ O ₆ Ru	C ₂₈ H ₁₈ Cl ₂ N ₂ O ₄ Ru
Formula weight	605.63	609.58	618.41
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P21/c	P21/c	P2/n
a (Å)	30.079(3)	12.7601(12)	8.8469(5)
b (Å)	16.7215(17)	12.0830(11)	12.7402(7)
c (Å)	11.3597(12)	20.8669(18)	12.3050(7)
α (°)	90	90	90
β (°)	92.1640(10)	123.198(3)	109.4820(10)
γ (°)	90	90	90
V (Å ³)	5709.5(10)	2692.2(4)	1307.51(13)
Ζ	8	4	2
D_{calc} (g cm ⁻³)	1.409	1.504	1.571
μ (mm ⁻¹)	0.588	0.629	0.841
F(000)	2480	1240	620
heta range (°)	2.29-25.02	2.55-25.02	2.374-28.325
Collected reflections	28125	13102	17707
Unique reflections	10053	4744	3204
R(int)	0.0547	0.0908	0.0190
Goodness-of-fit on F ²	1.066	1.059	1.037
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0484,$	$R_1 = 0.0511,$	$R_1 = 0.0253,$
	$wR_2 = 0.0933$	$wR_2 = 0.1044$	$wR_2 = 0.0786$
R indices (all data)	$R_1 = 0.0946$,	$R_1 = 0.0888,$	$R_1 = 0.0283,$
	$wR_2 = 0.1180$	$wR_2 = 0.1196$	$wR_2 = 0.0874$
Largest diff. peak and hole (e $Å^{-3}$)	0.548 and -0.771	1.047^{-} and -0.567^{-}	0.976 and -0.680

Table	1.	Crystal	data	and	summary	/ of	X-ray	data	collection	for	1–3.
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(ArC), 136.0 (ArC), 136.0 (ArC), 156.7 (ArC), 166.8 (ArC), 167.1 (N = CH), 195.2 (CO); IR (ν_{CO} , KBr, cm⁻¹): 2046 (s), 1972 (s).

2.5. General procedure for catalytic conversion of aldehydes to nitriles

In a 25 mL Schlenk tube, a mixture of benzaldehyde (0.106 g, 1.0 mmol), NH₂OH·HCl (0.07 g, 1.0 mmol), **1** (0.006 g, 0.01 mmol), toluene (5 mL) and NaHCO₃ (0.084 g, 1.0 mmol) was stirred at 110 °C for 10 h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and then concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography using ethyl acetate/petroleum ether to afford the pure product of benzonitrile.

2.6. X-ray crystallography

Single crystals of **1–3** suitable for X-ray diffraction were obtained by crystallization from CH₂Cl₂/*n*-hexane solution. Data collections were performed on a Bruker AXS SMART 1000 CCD diffractometer using graphite monochromated Mo K α radiation (φ/ω scan, $\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by fullmatrix least-squares. All calculations were done using the SHELXL program system. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced into calculated positions with the displacement factors of the host carbon atoms. CIF data were deposited as CCDC 1538115 (**1**), 1523387 (**2**) and 1504155 (**3**), respectively. A summary of crystal data and X-ray data collection for **1-3** is listed in Table 1.



Scheme 1. Synthesis of ruthenium carbonyl complexes 1–3.

3. Results and discussion

3.1. Synthesis and characterization of ruthenium(II) carbonyl complexes

Thermal treatment of phenoxy-imine ligands $RN = CHC_6H_4OH$ (L1: $R = 2,6-Me_2C_6H_3$; L2: R = 4-OMeC₆H₄; L3: R = 4-ClC₆H₄) with $Ru_3(CO)_{12}$ in a 5:1 molar ratio in refluxing toluene was performed to give the corresponding ruthenium(II) carbonyl complexes $[RN = CH(C_6H_4O)]_2Ru(CO)_2$ (1: $R = 2,6-Me_2C_6H_3$; 2: $R = 4-OMeC_6H_4$; 3: $R = 4-CIC_6H_4$) (Scheme 1). On varying the ratio of ligand L1: Ru₃(CO)₁₂ from 3: 1 to 6:1, the yield of 1 increased gradually and reached the highest yield in the ratio of 5:1. Then 2 and 3 were synthesized in the same ratio. The ¹H NMR spectra of ruthenium(II) complexes 1-3 shows singlets for their characteristic CH = N protons at 7.77, 8.06 and 7.98 ppm, respectively. It also indicates that the two molecules of ligands are in the same chemical environment. The signals in the range $6.55 \sim 7.42$ ppm can be attributed to their aromatic protons. The -OH protons at 12.78 ppm in the free ligands disappeared in all three complexes, suggesting that the phenoxy-imine ligands were successfully coordinated to the ruthenium center. Their ¹³C NMR spectra displayed a singlet around 195 ppm assigned to the carbonyl signals. The representative ¹³C NMR of **2** is given in Figure 1. In the IR spectra of 1-3, the strong absorption bands at 2040 cm⁻¹ and 1970 cm^{-1} also indicate the existence of two metal carbonyls.

3.2. X-ray structural studies

Crystals of **1–3** suitable for X-ray crystallography were grown by slow diffusion of *n*-hexane into CH_2Cl_2 solutions at ambient temperature. The molecular structures of **1–3** are depicted in Figures 2–4 and selected bond lengths and angles are given in Table 2. Complexes **1-3** crystallize in the monoclinic system with space group $P2_1/c$ for **1** and **2** and P2/n for **3**. X-ray diffraction analysis shows that all three ruthenium complexes are mononuclear structures and have a six-coordinate distorted octahedral geometry around the Ru metal center. The unit cell of **1** contains two crystallographically-independent molecules which possess similar connectivity and only one of them shown in Figure 2. The structures of the two crystallographically-independent molecules which posses similar connectivity and only one of them shown in Figure 2, the Ru ion was ligated by two molecules of phenoxy-imine ligands and the two carbonyls are situated in the *cis* position. The bond length of Ru(1)-O(1) [2.039(3) Å] is slightly shorter than the distance of Ru(1)-O(2) [2.048(3) Å] and also





Figure 2. Molecular structure of 1 with thermal ellipsoids drawn at the 30% level. All hydrogens are omitted for clarity.

shorter than the distances in complex $Ru_3(CO)_8(C_9H_6NO)_2$ [2.12 Å and 2.18 Å] [26]. The average Ru–N bond lengths are 2.098(4) Å and 2.092(4) Å, which are analogous to the values of 2.083(4) Å and 2.085(4) Å in **2** and 2.0929(18) Å in **3**. The Ru–C–O bond



Figure 3. Molecular structure of 2 with thermal ellipsoids drawn at the 30% level. All hydrogens are omitted for clarity.



Figure 4. Molecular structure of 3 with thermal ellipsoids drawn at the 30% level. All hydrogens are omitted for clarity.

angles [176.22(18) Å and 177.73(18) Å] are in the range of normal Ru–C–O bonds for ruthenium-carbonyl complexes [27, 28]. Complexes **2** and **3** display similar configurations which are chelated by two N,O-bidentate ligands and two CO groups. The Ru–N bond lengths of 2.083(4) Å and 2.085(4) Å for **2** and 2.092(4) Å for **3** are in agreement with the Ru–N bond length found in the complex RuCl(κ^2 –N,O–L–NO₂)(CO)(PPh₃)₂ [2.113(3) Å] [29] and are relatively longer than the values [2.035(4) Å and 2.052(4) Å] observed in complex [RuCl(PPh₃)(salpn)]·CH₂Cl₂ [30]. Complex **3** is symmetrical molecule in which the Ru–O, Ru–N lengths and Ru–C–O bond angles are similar to the reported literatures [29, 31, 32]. As shown in Figure 5, the packing of **1–3** was controlled by weak intermolecular C–H…O hydrogen bonding interactions, where the

Table 2. Selected bond lengths (Å) and angles (°) for 1–3.

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1			
Ru(1)-C(31)	1.872(7)	Ru(1)-C(32)	1.866(7)
Ru(1)-O(1)	2.069(4)	Ru(1)-O(2)	2.058(4)
Ru(1)-N(1)	2.160(4)	Ru(1)-N(2)	2.095(5)
C(32)-Ru(1)-O(1)	177.2(2)	C(32)-Ru(1)-O(2)	92.8(2)
C(31)-Ru(1)-O(1)	93.0(2)	O(2)-Ru(1)-O(1)	84.98(16)
O(2)-Ru(1)-N(2)	89.01(18)	O(1)-Ru(1)-N(2)	83.39(17)
C(31)-Ru(1)-N(1)	97.3(2)	N(2)-Ru(1)-N(1)	166.92(18)
O(2)-Ru(1)-N(1)	80.45(17)	O(1)-Ru(1)-N(1)	87.96(16)
2			
Ru(1)-O(1)	2.050(3)	Ru(1)-O(3)	2.054(3)
Ru(1)-N(1)	2.085(4)	Ru(1)-N(2)	2.083(4)
C(30)-Ru(1)-O(1)	173.98(18)	C(29)-Ru(1)-O(1)	91.99(19)
C(29)-Ru(1)-O(3)	173.53(16)	O(1)-Ru(1)-O(3)	83.95(13)
O(1)-Ru(1)-N(2)	84.54(13)	O(3)-Ru(1)-N(2)	90.93(14)
C(30)-Ru(1)-N(1)	93.55(19)	N(2)-Ru(1)-N(1)	173.56(14)
O(1)-Ru(1)-N(1)	90.77(15)	O(3)-Ru(1)-N(1)	84.18(13)
3			
Ru(1)-O(2)	2.0552(13)	Ru(1)-N(1)	2.0929(18)
C(1)-Ru(1)-O(2)	174.76(5)	C(1)-Ru(1)-N(1)	95.65(7)
O(2)-Ru(1)-N(1)	88.79(6)	C(2)-O(2)-Ru(1)	126.18(12)
C(8)-N(1)-Ru(1)	123.03(13)	C(9)-N(1)-Ru(1)	121.03(13)
N(1i)-Ru(1)-N(1)	173.03(7)	O(2i)-Ru(1)-N(1)	86.09(5)
O(2)-Ru(1)-O(2i)	85.57(8)	O(2i)-Ru(1)-N(1i)	88.80(6)



Figure 5. Crystal packing of 1–3 showing intermolecular hydrogen bonds as dashed lines.

Catalyst, base

R = Me, OMe, Cl, Br etc.

Scheme 2. Catalytic conversion of aldehydes to corresponding nitriles.

Table 3. Screening of different solvents and bases for the synthesis of nitriles catalyzed by ruthenium complex 1.^a

Entry	Solvent	Base	Yield ^b (%)
1	CH₃CN	NaHCO ₃	70
2	Toluene	NaHCO ₃	79
3	C₂H₅OH	NaHCO ₃	60
4	CH ₂ Cl ₂	NaHCO ₃	57
5	DMSO	NaHCO ₃	14
6	DMF	NaHCO ₃	46
7	Toluene	Na ₂ CO ₃	65
8	Toluene	NaOH	51
9	Toluene	КОН	54
10	Toluene	NaOAc	62
11	Toluene	t-BuOK	37

^aReaction conditions: benzaldehyde (1.0 mmol), NH₂OH·HCl (1.0 mmol), base (1.0 mmol), catalyst 1 (1.0 mol%) and solvent (5.0 mL).

^blsolated yield.

Entry	Catalyst	Temp. (°C)	Time (h)	Yield ^b (%)
1	1	110	10	79
2	2	110	10	84
3	3	110	10	65
4	2	90	10	70
5	2	110	15	85
6	2	110	8	72
7	_	110	10	52
8 ^c	2	110	10	18

Table 4. Conversion of benzaldehyde to benzonitrile using 1-3.^a

^aReaction conditions: benzaldehyde (1.0 mmol), NH₂OH HCl (1.0 mmol), NaHCO₃ (1.0 mmol), catalyst (1.0 mol %) and toluene (5.0 mL).

^blsolated yield.

^cWithout NaHCO₃.

benzene ring protons are involved in intermolecular hydrogen bonding interactions with the phenoxy oxygen atoms.

3.3. Catalytic conversion of aldehydes to nitriles

Ruthenium(II) carbonyl complexes **1–3** have been used as catalysts to catalyze conversion of aromatic aldehydes to the corresponding nitriles in different solvents in the presence of base (Scheme 2). Initial experiments were carried out to find the most suitable solvent and base by means of benzaldehyde as model substrate and **1** as catalyst. As shown in Table 3, ruthenium(II) complex **1** was found to be active toward the transformation of benzaldehyde to benzonitrile in toluene, acetonitrile and ethanol but showed less active in dichloromethane, DMSO and DMF (Table 3, entries 1-6). The catalyst activity is strongly solvent-dependent and toluene is the best medium to give

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Entry	Substrate	Product	Yield ^b (%)
1	ОН	CN	77
2	MeO	MeO	73
3	CI	CI	65
4	Br	Br	57
5	O ₂ N H	O ₂ N CN	60
6	НО	HO	47

 Table 5. Screening of substrates for nitriles synthesis catalyzed by ruthenium complex 2.^a

^aReaction conditions: aldehyde (1.0 mmol), NH₂OH·HCI (1.0 mmol), NaHCO₃ (1.0 mmol), catalyst (1.0 mol %) and toluene (5.0 mL). ^bIsolated yield.

benzonitrile in 79% yield. By varying the bases in catalytic reactions, the highest yield of the desired product was achieved in the presence of NaHCO₃ compared to the others (Na₂CO₃, NaOH, KOH, Na₂OAc and *t*-BuOK, 37-65% yields) (Table 3, entries 7–10).

Complexes **1–3** were then investigated to optimize the best catalyst and the results are summarized in Table 3. Among the different complexes, **2** having an electrondonating group (viz. OMe) showed the highest activity, giving the corresponding benzonitrile in an excellent yield of 84% (Table 4, entry 2). Analogously, **3** bearing a chloro-substituted ligand displayed lower catalytic activity than **1** and **2** (Table 4, entry 3). When the reaction was carried out at 90 °C, the yield of the desired product dropped into 70% (Table 4, entry 4). Hence, a refluxing temperature of 110 °C was necessary to maintain the catalytic activity. Further extending the reaction time to 15 h did not significantly increase the yield of acetonitrile and the yield was decreased to 72% when the reaction was reduced to 8 h (Table 4, entries 5 and 6). The optimizing reaction time was determined to be 10 h. Finally, the control experiments showed that 52% yield of the acetonitrile was obtained without the catalyst and just 18% was achieved in the absence of NaHCO₃ (Table 4, entries 7 and 8), indicating that both catalyst and base are crucial to convert benzaldehyde to acetonitrile as well as eliminate HCl and water.

To explore the scope of the present catalytic system, reactions of various aldehydes were conducted using catalyst **2** under the optimized conditions. As shown in Table 5, several substituted benzonitriles were successfully synthesized with moderate to good isolated yields using the above optimized protocol. Electron-donating groups, such as $-CH_3$, $-OCH_3$ and -OH (entries 1, 2 and 6), and electron-withdrawing substituents, such as the -CI, -Br and $-NO_2$ (entries 3-5), on the benzaldehyde moiety altered the reactions and the corresponding nitriles were obtained in the yields of 47-77%. The substituted benzonitriles gave slightly lower yields compared with benzaldehyde, indicating the present catalytic system was somewhat sensitive to the functional groups.

4. Conclusion

Mononuclear ruthenium(II) carbonyl complexes **1–3** bearing two phenoxy-imine ligands have been synthesized and well characterized by elemental analysis, IR, NMR spectroscopy and X-ray crystal diffraction analysis. In the presence of NaHCO₃, these ruthenium(II) complexes were employed as the catalysts for conversion of aldehydes and NH₂OH·HCl to the corresponding nitriles in moderate to good yields *via* the dehydration of aldoximes. The present work offers an alternative route for synthesis of nitriles in one pot catalyzed by transition metal carbonyl complexes.

Disclosure statement

No potential conflict of interest was reported by the authors.

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