



Ruthenium hydride complex supported on multi-wall carbon nanotubes for catalytic C–C bond formation *via* transfer hydrogenation

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ABSTRACT

In this work, the preparation, characterization and investigation of catalytic activity ruthenium hydride catalyst, $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$, supported on MWCNT in the synthesis of β,γ -unsaturated ketones *via* carbon–carbon bond formation are reported. In the first reaction step, the MWCNTs were modified with 1,2-ethanedithiol, and in a second reaction step, the catalyst was attached to MWCNTs *via* this linker. The catalyst was characterized by diffuse reflectance UV–vis and FT-IR spectroscopic techniques, SEM, ICP and elemental analysis methods. The catalyst was reused several times without significant loss of its catalytic activity.

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1. Introduction

The formation of carbon–carbon bond has received much attention in chemical transformation specially for construction of molecular frameworks with increasing complexity [1–7]. Many reports have been focused on the direct coupling of diverse π -unsaturated compounds such as allenes [8–10], alkynes [3,11], enones [12–14], dienes [15–19] and enynes [2] with conventional electrophiles, particularly carbonyl compounds, catalyzed by homogenous metal catalysts. Ruthenium based complexes are generally considered to be reactive toward these reactions. Despite the high reactivity of ruthenium complexes in organic synthesis, the difficulty of their reusability and stability limits their practical applications. To overcome these problems, ruthenium catalysts have been immobilized on different types of supports [20–27].

Carbon nanotubes (CNTs) have attracted much attention in the synthesis, characterization, and applications because of their unique structural, mechanical, thermal and electronical properties. Due to the above-mentioned properties, and also high surface area of CNTs and their insolubility in the most solvents, these materials can be used as catalysts support [28–30]. For example, PtNi alloy nanoparticles supported on functionalized multi-wall carbon

nanotube/polysiloxane composite films for methanol electro-oxidation [31], palladium supported on single-wall carbon nanotubes for Heck and Suzuki couplings, aerobic oxidation of alcohol and selective hydrogenation [32], Pd-CNT for Suzuki coupling [33], CNT supported cobalt for CO oxidation [34], Pd-CNT for hydrodehalogenation of aryl halides [35], Pt nanoparticles supported on CNTs have been used for methanol oxidation [36], palladium nanoparticles supported on CNTs for semihydrogenation of phenylacetylene [37], chiral vanadylsalen complex supported on single-wall CNTs for enantioselective cyanosilylation of aldehydes [38,39], manganese(III) porphyrin and manganese(III) salophen supported on MWCNTs for epoxidation of alkenes with NaIO_4 [40,41] and molybdenum and tungsten hexacarbonyl supported on MWCNTs for alkenes epoxidation with *tert*-BuOOH [42,43].

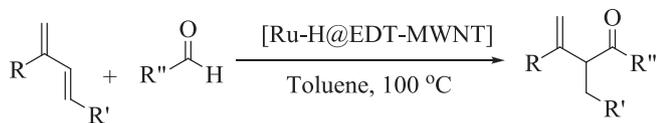
On the other hand, immobilization of catalysts on MWCNT can improve specific properties such as selectivity and conversion, catalytic activity, reduce the reaction time, stability, corrosion resistance in electrocatalysts, easier separation and satisfactory reusability, which shows the use of CNTs as support is a suitable selection [44–48].

Recently, homogeneous ruthenium hydride catalyst has been used for transfer hydrogenation of dienes with alcohols and aldehydes [17,18]. To develop this investigation, here, we report the application of $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ supported on MWCNT for catalytic C–C bond formation *via* transfer hydrogenation (Scheme 1). The catalyst was characterized by elemental analysis, FT-IR and diffuse reflectance UV–vis spectroscopic methods and SEM technique.

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Scheme 1. Synthesis of unsaturated ketones catalyzed by $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ supported on MWCNT.

Table 1

The specification of MWCNT-COOH used in this study.

MWCNT-COOH				
Outside diameter (nm)	Inside diameter (nm)	Length (μm)	COOH content (%)	Specific surface area (m^2/g)
20–30	5–10	30	1.5	>110

2. Experimental

All materials were commercial reagent grade and obtained from Merck and Fluka chemical companies. Elemental analysis was performed on a Perkin–Elmer 2400 instrument. Atomic absorption analyses were carried out on a Shimadzu 120 spectrophotometer. Diffuse reflectance spectra were recorded on a Shimadzu UV-265 instrument using optical grade BaSO_4 as reference. FT-IR spectra were obtained as potassium bromide pellets in the range $500\text{--}4000\text{ cm}^{-1}$ with a Bomen–Hartmann instrument. Scanning electron micrographs of the support and catalyst were taken on a SEM EM 3200 instrument. ^1H NMR spectra were recorded on a Bruker-Avance AQS 400 MHz. The ICP analyses were performed on an ICP-Spectrociros CCD instrument. Mass spectra were recorded on a Platform II spectrometer from Micromass, EI mode at 70 eV. Solvents and aldehydes were distilled prior to use. The products were purified by silica gel chromatography (Merck KGaA, Silica Gel 60). The MWCNTs containing carboxylic acid groups were purchased from Shenzhen NTP Factory (China). Table 1 shows the characteristics of these MWCNTs. The $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ complex was prepared according to the method reported in the literature [49].

2.1. Preparation of the supports

2.1.1. Preparation of the MWCNT modified with 1,2-ethanedithiol, EDT-MWCNT

First, carboxylic acid groups were converted to thiol groups $[-\text{COS}(\text{CH}_2)_2\text{SH}]$, according to a previously reported method

[50]. The carboxylated MWCNTs and 1,2-ethanedithiol (EDT) as linker were mixed in THF and the mixture was stirred at $50\text{ }^\circ\text{C}$ for 12 h. Then the reaction mixture was cooled to room temperature and filtered. The solid EDT-MWCNT was washed with THF and dried.

2.1.2. Preparation of the MWCNT modified with different amines, MWCNT-amine

For attachment of the amines to MWCNTs, the MWCNT-COOH was converted to MWCNT-COCl [43]. In a 50 ml round-bottom flask equipped with a magnetic stirring bar, MWCNT-COCl (1 g) and Et_3N (1 mL) were added to a solution of amine (0.5 g) in dimethyl formamide (DMF) (20 mL) and heated at $80\text{ }^\circ\text{C}$ for 24 h. Then, the reaction mixture was filtered, washed with CH_3CN and dried at $60\text{ }^\circ\text{C}$.

2.2. Preparation of the catalyst $[\text{Ru-H@EDT-MWCNT}]$

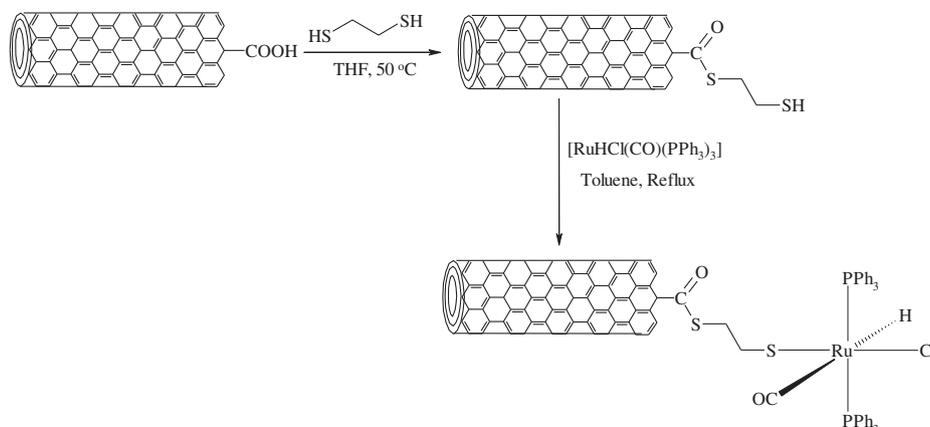
For attachment of catalyst to support, the EDT-MWCNT (1 g) was dispersed in anhydrous toluene (50 mL) by vigorous stirring, and a solution of $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ (0.2 g) in anhydrous toluene (10 mL) was added to this mixture. The mixture was refluxed for 24 h, the $[\text{Ru-H@EDT-MWCNT}]$ was filtered, washed with toluene to remove the excess reactants and dried under vacuum for 24 h. A similar procedure was applied for attachment of $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ to amine modified MWCNT.

2.3. Synthesis of 2,3-dimethyl-1-phenylbut-3-en-1-one catalyzed by $[\text{Ru-H@EDT-MWCNT}]$

Freshly distilled benzaldehyde (**1a**, 108 mg, 1 mmol), isoprene (**2a**, 340.7 mg, 4 mmol), $[\text{Ru-H@EDT-MWCNT}]$ (8 mol%, 400 mg.) and toluene (6 mL) were placed in a screw capped test tube. The test tube was purged with argon and sealed. The mixture was stirred at $100\text{ }^\circ\text{C}$ for 16 h. After the reaction was completed, the catalyst was filtered and washed with EtOH (10 ml). The solvent was evaporated under reduced pressure and the residue was purified by chromatography on a silica gel plate (petroleum ether/ethyl acetate = 50/1) to give 2,3-dimethyl-1-phenylbut-3-en-1-one (**3a**, 161 mg, 90%).

2.4. General procedure for the synthesis of α,β - and β,γ -unsaturated ketones

In a screw capped test tube, freshly distilled aldehyde (**1**, 1 mmol), diene (**2**, 4 mmol), $[\text{Ru-H@EDT-MWCNT}]$ (8 mol%, 400 mg.) were



Scheme 2. The preparation route for catalyst.

added toluene (6 mL). The test tube was purged with argon and sealed. The reaction mixture was allowed to stir at 100 °C for 16 h. After the reaction was completed, the catalyst was filtered and washed with EtOH (10 ml). The solvent was evaporated under reduced pressure and the residue was purified by chromatography on a silica gel plate (petroleum ether/ethyl acetate = 50/1) to give desired product.

3. Results and discussion

3.1. Catalyst preparation and characterization

Scheme 2 shows the preparation route for catalyst. The modified MWCNT, EDT-MWCNT, was prepared by the reaction of 1,2-ethanedithiol with MWCNT-COOH via a thioester linkage. The [Ru-H@EDT-MWCNT] catalyst was prepared by the reaction of EDT-MWCNT with a solution of [RuHCl(CO)(PPh₃)₃]. The [Ru-H@EDT-MWCNT] catalyst was characterized by elemental analysis, spectroscopic methods and SEM. The sulfur content of the support was 9.43%. According to this value, the amount of S which is available for attachment of [RuHCl(CO)(PPh₃)₃] is about 1.47 mmol/g. The amount of Ru in the supported catalyst, determined by ICP, was about 2.1% (0.2 mmol/g). The FT-IR spectra of [RuHCl(CO)(PPh₃)₃] showed characteristic bands at 2013 cm⁻¹(Ru–H) and 1925 cm⁻¹

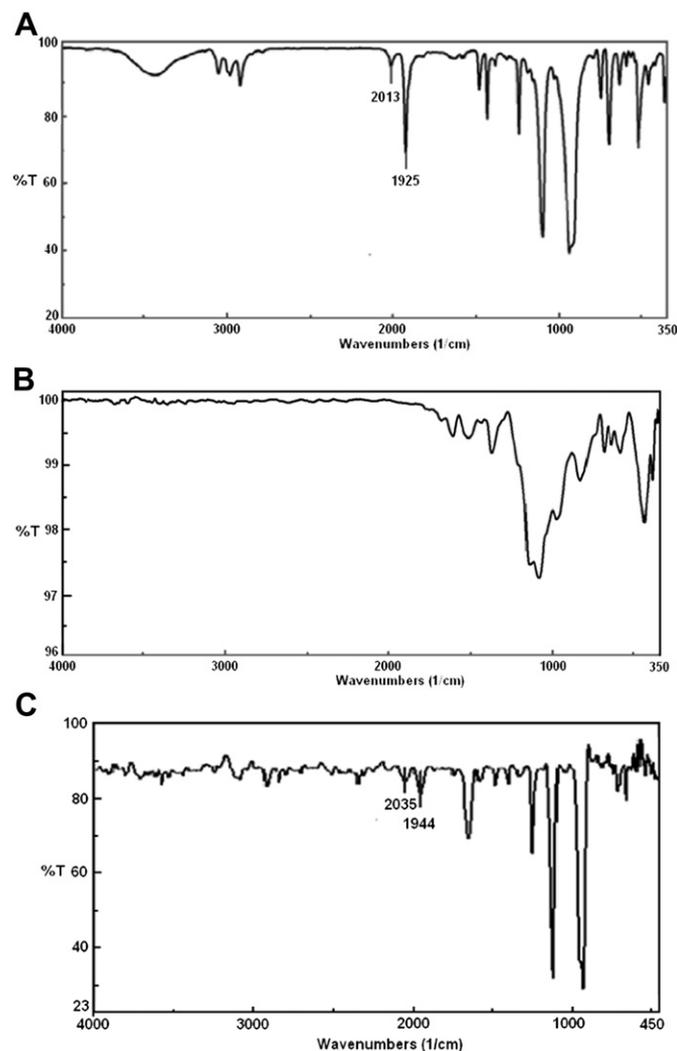


Fig. 1. FT-IR spectrum of: (A) [RuHCl(CO)(PPh₃)₃], (B) MWNT-SH and (C) [Ru-H@EDT-MWNT].

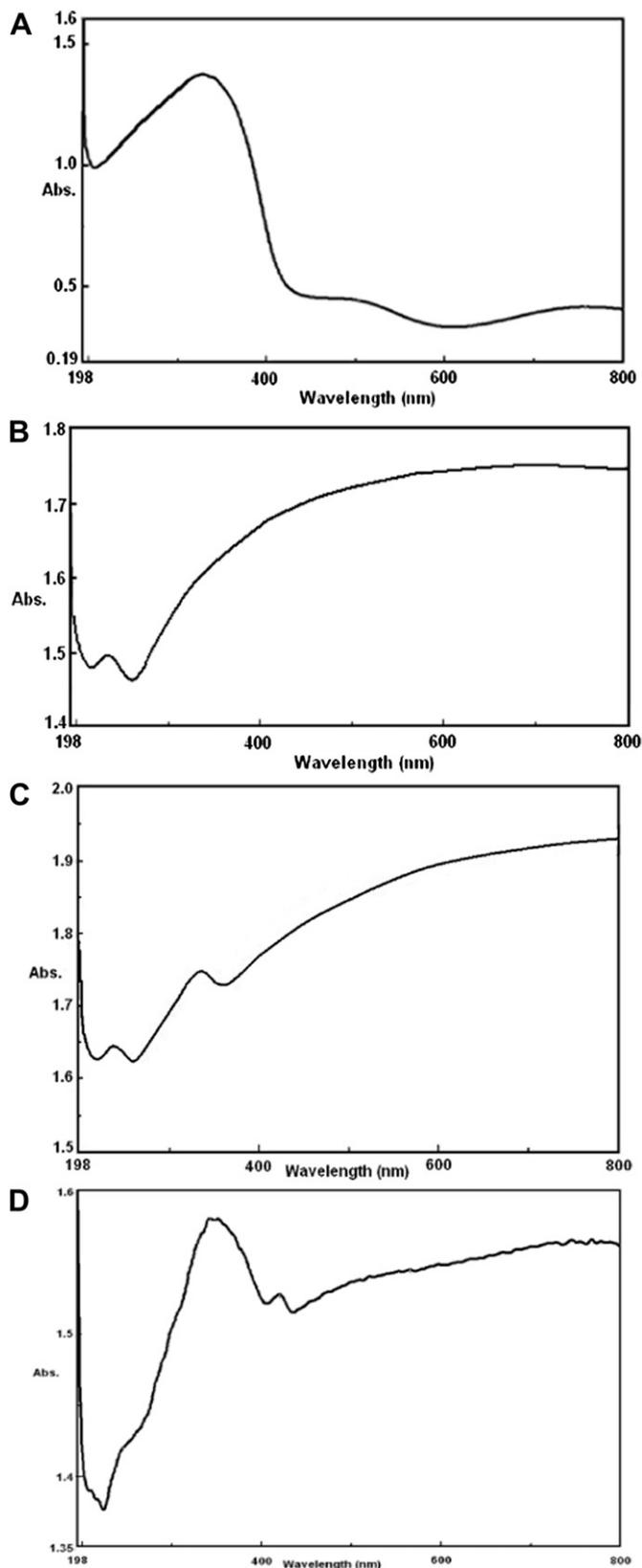


Fig. 2. DR UV-vis spectrum of: (A) [RuHCl(CO)(PPh₃)₃], (B) MWNT-SH, (C) [Ru-H@EDT-MWNT] and (D) [RuHCl(CO)(PPh₃)₃] + MWCNTs.

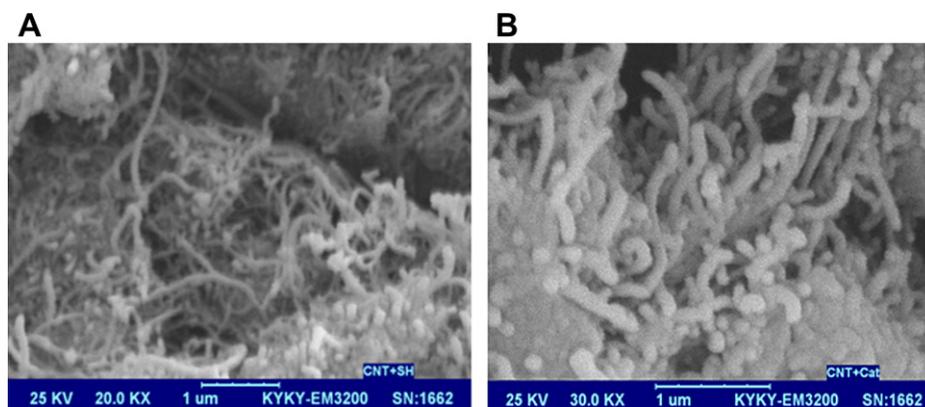


Fig. 3. SEM image of: (A) MWNT-SH and (B) [Ru-H@EDT-MWNT].

(C=O) which shifted to 2035 and 1944 cm^{-1} , respectively, upon immobilization (Fig. 1), while MWCNTs show no band in this region. These absorption peaks indicate that ruthenium complex has been successfully supported on the MWNTs surface.

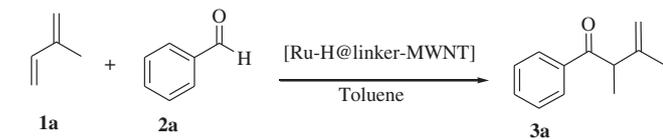
The UV–vis spectra of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$, EDT-MWNT and [Ru-H@EDT-MWNT] in the diffuse reflectance mode are shown in Fig. 2. The homogeneous ruthenium hydride complex has a characteristic absorption peak at 329 nm (Fig. 2A). The EDT-MWNT exhibits an absorption peak at 237 nm (Fig. 2B), whereas the [Ru-H@EDT-MWNT] showed two peaks at 240 nm (corresponds to the support) and 341 nm (Fig. 2C). The latter is attributed to the Ru complex with a bathochromic shift in comparison with the non-supported complex. The diffuse UV–vis spectrum of a mixture of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ and MWCNTs was also recorded. As can be seen in Fig. 2D, this spectrum is as same as homogeneous $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ spectrum. While the spectrum of [Ru-H@EDT-MWNT] shows that the coordination sphere may be different.

The SEM images of the [Ru-H@EDT-MWNT] showed that the nanotubes are aggregated and has retained their nanotube nature upon functionalization with EDT and support of catalyst on them (Fig. 3).

3.2. Synthesis of β,γ -unsaturated ketones

First, we examined the effect of different linkers and it was observed that 1,2-ethanedithiol was the best linker for attachment

Table 2
Effect of different linkers in the reaction of isoprene with benzaldehyde.^a



Entry	Linker	Yield (%) ^b
1	$\text{H}_2\text{N}(\text{CH}_2)_2\text{SH}$	50
2		10
3	$\text{H}_2\text{N}(\text{CH}_2)_2\text{OH}$	20
4	$\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2$	35
5	$\text{HS}(\text{CH}_2)_2\text{SH}$	90
6	No linker	8

^a All reactions were performed using **1a** (4 mmol), **2a** (1 mmol), supported catalyst (8 mol%), and toluene (6 mL) in a screw test tube at 100 °C for 16 h.

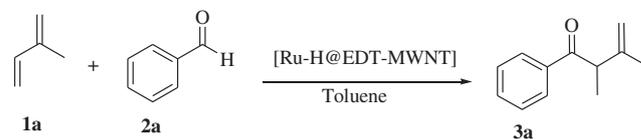
^b Isolated yield.

of Ru catalyst to MWCNTs in which the highest yield was observed in the reaction of isoprene (**1a**) with benzaldehyde (**2a**) as model reaction (Table 2). To check whether the reaction is catalyzed by covalent attached or adsorbed $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$, a mixture of MWCNTs with $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ was refluxed in toluene for 24 h and filtered. This catalyst was used in the model reaction. The results showed that only 8% of the 2,3-dimethyl-1-phenylbut-3-en-1-one was produced. This shows that the amount of adsorbed catalyst is too low to catalyze the reaction.

Then, the reaction parameters such as catalyst amount, kind of solvent and temperature were optimized in the model reaction. Initial studies were focused on the coupling of isoprene (**1a**) with benzaldehyde (**2a**) for the optimization of reaction conditions (Table 3). The results showed that 8 mol% of [Ru-H@EDT-MWNT] efficiently catalyzed the model reaction at 100 °C in toluene to give the 2,3-dimethyl-1-phenylbut-3-en-1-one (**3a**) (Table 3, entry 3). The effect of different solvents was also investigated in the model reaction. As can be seen, the highest yield was obtained using toluene as reaction media. The effect of temperature was also checked on the model reaction. The results showed that increasing the temperature higher than 100 °C did not affect the yield (entry 8).

The applicability and generality of this method were examined using a variety of dienes and aldehydes (Table 4). The reaction of isoprene (**1a**) with benzaldehyde and substituted benzaldehydes **2** bearing electron-donating substituents (methyl and methoxy) and electron-withdrawing groups (bromo, fluoro, cyano and nitro)

Table 3
Optimization of conditions in the reaction of **1a** with **2a**.^a



Entry	Catalyst amount (mol%)	Solvent	Temperature	Yield (%) ^b
1	4	Toluene	100	60
2	6	Toluene	100	78
3	8	Toluene	100	90
4	10	Toluene	100	90
5	8	1,2-Dichloroethane	80	53
6	8	THF	90	30
7	8	Toluene	90	80
8	8	Toluene	110	90

^a All reactions were performed using **1a** (4 mmol), **2a** (1 mmol), supported catalyst, and solvent (6 mL) in a screw test tube for 16 h.

^b Isolated yield.

Table 4
Synthesis of unsaturated ketones catalyzed by [Ru-H@EDT-MWCNT].^a

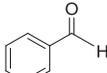
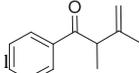
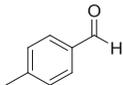
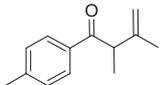
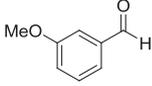
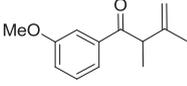
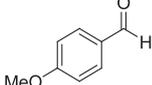
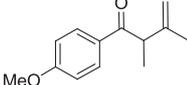
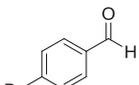
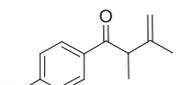
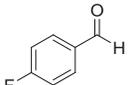
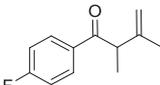
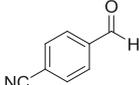
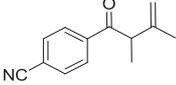
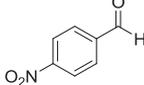
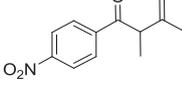
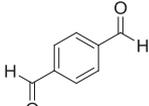
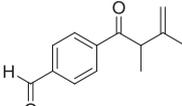
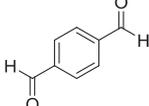
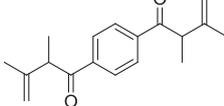
Entry	Diene 1	Aldehyde 2	Unsaturated ketones 3	Yield (%) ^b	[Ru-H@EDT-MWCNT]		[RuHCl(CO)(PPh ₃) ₃] [18]	
					TON	TOF (h ⁻¹)	TON	TOF (h ⁻¹)
1	 1a	 2a	 3a	90	11.25	0.70	16.2	0.67
2	1a	 2b	 3b	80	10.00	0.62	15.6	0.65
3	1a	 2c	 3c	92	11.50	0.72	18.8	0.78
4	1a	 2d	 3d	70	8.75	0.55	14	0.58
5	1a	 2e	 3e	68	8.50	0.53	–	–
6	1a	 2f	 3f	73	9.10	0.57	12.4	0.52
7	1a	 2g	 3g	92	11.50	0.72	–	–
8	1a	 2h	 3h	95	11.87	0.74	–	–
9	1a	 2i	 3i	87	10.87	0.68	–	–
10 ^c	1a	 2i	 3j	82	5.12	0.32	–	–

Table 4 (continued)

Entry	Diene 1	Aldehyde 2	Unsaturated ketones 3	Yield (%) ^b	[Ru-H@EDT-MWCNT]		[RuHCl(CO)(PPh ₃) ₃] [18]	
					TON	TOF (h ⁻¹)	TON	TOF (h ⁻¹)
11	1a	2j	3k	85	10.62	0.66	–	–
12	1b	2g	3l	81	10.12	0.63	–	–
13	1b	2h	3m	83	10.37	0.65	–	–
14	1b	2k	3n (E/Z = 48/52)	79	9.87	0.62	–	–
15	1c	2d	3o (E/Z = 49/51)	84	10.50	0.66	–	–

^a All reactions were performed using **1** (4 mmol), **2** (1 mmol), supported catalyst (8 mol%) and toluene (6 mL) in a screw test tube for 16 h.

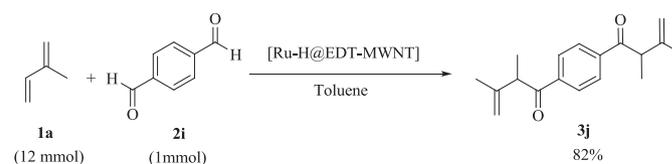
^b Isolated yield.

^c Reaction was performed using **1a** (8 mmol), **2i** (1 mmol), supported catalyst (16 mol%) and toluene (10 mL) in a screw test tube for 16 h (See Scheme 2).

produced the corresponding β,γ -unsaturated ketones **3** with good to excellent yields at 100 °C in toluene and in the presence of 0.08 mmol of [Ru-H@EDT-MWCNT] (entries 1–8). An excellent selectivity was observed in the reaction of terephthalaldehyde (**2i**) with isoprene (**1a**). When 1 mmol of terephthalaldehyde (**2i**) was reacted with 4 mmol of isoprene (**1a**) (entry 9) in the presence of 0.08 mmol of catalyst, only one aldehydic group was reacted and the other was remained intact, and the 4-(2,3-dimethyl-but-3-enoyl)-benzaldehyde (**3j**) was obtained in 87% yield. On the other hand, when the same reaction was carried out with 12 mmol of isoprene (**1a**) and in the presence of 16 mol% of catalyst, both aldehydic groups were reacted and 1,4-bis(2,3-dimethyl-but-3-enoyl)benzene (**3j**) was produced in 82% yield (Scheme 3). The reaction of indol-3-carbaldehyde (**2j**), as a heteroaromatic aldehyde, with isoprene (**1a**) was also investigated and the corresponding unsaturated ketone (**3k**) was produced in 85% yield (entry 11). Since the ruthenium hydride catalyst has been employed for double bond isomerization [51], we tested the reactivity of 1,5-hexadiene (**1b**) in cross-coupling reaction. Interestingly, in the

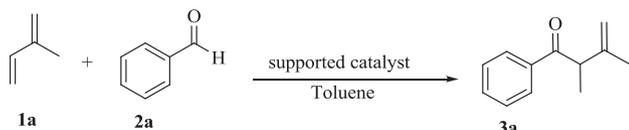
reaction of 4-cyanobenzaldehyde (**2g**) and 4-nitrobenzaldehyde (**2h**) with 1,5-hexadiene (**1b**) and in the presence of [Ru-H@EDT-MWCNT], only the Z isomers (**3l** and **3m**) were obtained (entries 12 and 13). But in the reaction of thiophene-3-carbaldehyde (**2k**) with 1,5-hexadiene (**1b**), the α,β -unsaturated ketone (**3n**) was obtained as a 48/52 mixture of E/Z isomers (entry 14). When 1,3-cyclooctadiene (**1c**) was used as diene, a 49/51 mixture of E/Z isomers (**3o**) was produced (entry 15).

The study of the reactivity of aldehydes in Table 4 showed that aldehydes constitute electron-withdrawing substituents was more



Scheme 3. Synthesis of 1,4-bis(2,3-dimethyl-but-3-enoyl)benzene.

Table 5
Effect of different supported catalyst in the reaction of isoprene with benzaldehyde.^a



Entry	Supported Catalyst	Yield (%) ^b
1	[Ru-H@EDT-MWCNT]	90
2	[Ru-H@EDT-AuNP]	32
3	[Ru-H@Nano-silica]	8

^a Both reactions were performed using **1a** (4 mmol), **2a** (1 mmol), supported catalyst (8 mol%), and toluene (6 mL) in a screw test tube at 100 °C for 16 h.

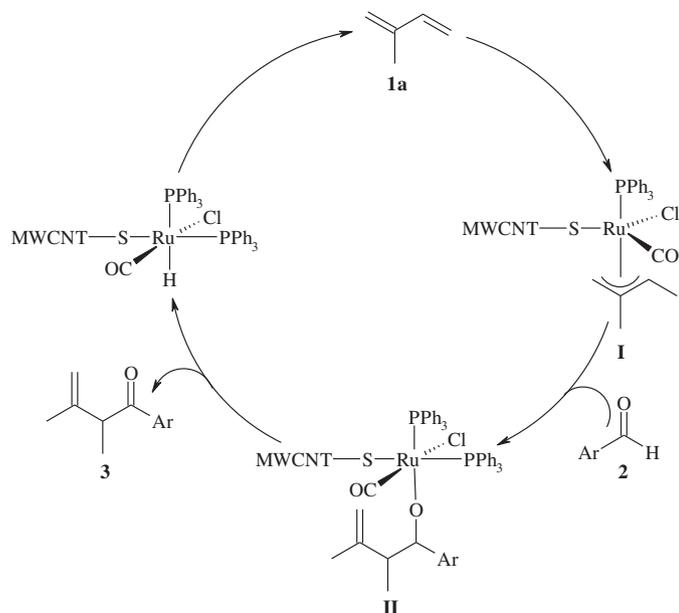
^b Isolated yield.

reactive than aldehydes bearing electron-donating groups and gave the desired products in higher yields. It seems that electron-donating groups stabilize the parent aldehydes *via* resonance and therefore, the reaction rate and the yields reduce.

The catalytic activity of RuHCl(CO)(PPh₃)₃ supported on gold nanoparticles (AuNP) and nano-silica was also investigated in the reaction of isoprene (**1a**) with benzaldehyde (**2a**) (Table 5). As can be seen, these heterogeneous catalysts are less efficient than [Ru-H@EDT-MWCNT]. During the reaction, the [Ru-H@EDT-MWCNT] particles are suspended in the solvent. This is due to the bundled agglomerates of MWCNT that aggregate slowly and make the catalyst suspend in the reaction mixture for a long period of time. While, other heterogeneous catalysts were aggregated more rapidly in comparison with CNTs.

For comparison of catalytic activity of this catalyst with homogeneous counterpart, the TONs and TOFs were calculated (Table 5). As can be seen, despite higher TONs for homogeneous catalyst, the TOFs for heterogeneous catalyst are comparable to homogeneous catalyst.

Since the identification of intermediates was not possible; therefore, a mechanism is reported on the basis of homogeneous conditions [18]. As mentioned previously, the supported Ru catalyst reacts with diene **1a** to produce the π -allyl complex **I**. Addition of



Scheme 4. The reaction pathway.

Table 6
The results of [Ru-H@EDT-MWCNT] catalyst recovery and the amount of Ru leached in the reaction of benzaldehyde (**2a**) with isoprene (**1a**).

Row	Yield (%) ^a	Ru leached (%) ^b
1	90	1.1
2	86	0.8
3	83	0
4	76	0

^a Isolated yield.

^b Determined by atomic absorption spectroscopy.

aldehyde **2** to this π -complex gives the intermediate **II**, which in turns produces the unsaturated ketone compound **3** and releases the catalyst for the next catalytic cycle (Scheme 4).

3.3. Catalyst reuse

The reusability of the [Ru-H@EDT-MWCNT] was checked using multiple sequential reaction of benzaldehyde (**2a**) with isoprene (**1a**). For each of the repeated reactions, the catalyst was recovered, washed exhaustively with diethyl ether, and dried before being used with fresh benzaldehyde **2a** with isoprene **1a**. The results showed that the catalyst was consecutively reused four times without a significant loss in its activity (Table 6).

On the other hand, the reaction was stopped at half conversion and the half of the volume with the material was filtered at 100 °C (reaction temperature). Execution of the reaction under the same reaction conditions, as with catalyst, showed no significant conversion and only 5% of 2,3-dimethyl-1-phenylbut-3-en-1-one was produced. These observations show the strong attachment of RuHCl(CO)(PPh₃)₃ to MWCNT *via* 1,2-ethanedithiol.

4. Conclusion

In conclusion, [Ru-H@EDT-MWCNT] was successfully supported on 1,2-ethanedithiol functionalized MWCNTs and characterized. This heterogeneous catalyst was used for preparation of unsaturated ketones by the reaction of dienes with aldehydes. The catalyst was reused several times without significant loss of its catalytic activity.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jorganchem.2012.10.028>.

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