



A highly efficient synthesis of oxindoles using a functionalized silica gel as support for indium(III) acetylacetonate catalyst in an aqueous-acetonitrile medium

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ARTICLE INFO

Article history:

Received 24 March 2010
Received in revised form 5 August 2010
Accepted 24 August 2010
Available online 24 September 2010

Keywords:

Indium(III) acetylacetonate complex
Functionalized
Silica gel
Oxindoles
13C-CPMAS spectral studies

ABSTRACT

Aminopropylsilica gel (APSG) was obtained by the modification of silica gel with 3-aminopropyltriethoxy silane. The indium(III) acetylacetonate complex was then subsequently anchored to yield In(acac)₃-bonded silica gel (In(acac)₃-APSG). The structure was investigated and confirmed by surface area (BET), elemental and thermogravimetric analyses, FT-IR, ¹³C-CPMAS spectral studies and inductively coupled plasma mass spectrometry technique (ICP-MS). The new In(acac)₃-APSG material was tested in the synthesis of oxindoles derivatives that were synthesized via the electrophilic substitution reaction of indoles with various isatins in water. The catalyst is highly stable and recyclable for several times. The work-up procedure is very simple and oxindoles were obtained in high yields.

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1. Introduction

With the increasing awareness of green chemistry there has been a tremendous pressure on chemical industries to develop environmentally friendly processes [1]. The separation of product/catalyst from the reaction mixture is one of the major contributors to waste in chemical processes. This stage often generates large volumes of waste effluent. Also, the process of extracting the catalyst can often destroy the catalyst. Thus, elimination of this step would be favourable and is one of the major goals of green chemistry [2].

In this context, heterogeneous catalysis is emerging as an alternative to homogeneous processes since catalysts can be recovered after the reaction and re-used several times to achieve very high turnover numbers [3]. In fact, the last decade has witnessed a growing interest in building organic–inorganic hybrid catalysts using several types of supports and several immobilization strategies [4–12]. One strategy to transform a homogeneous into heterogeneous process is to anchor the active site onto a large surface solid carrier provided that the anchoring methodology maintains the intrinsic activity and selectivity of the catalytic centre [13]. Among various solid supports, silica is usually preferred since it displays many advantageous properties such as high surface area, excellent

stability (chemical and thermal), good accessibility, and organic groups can be robustly anchored to the surface, to provide catalytic centres [13,14].

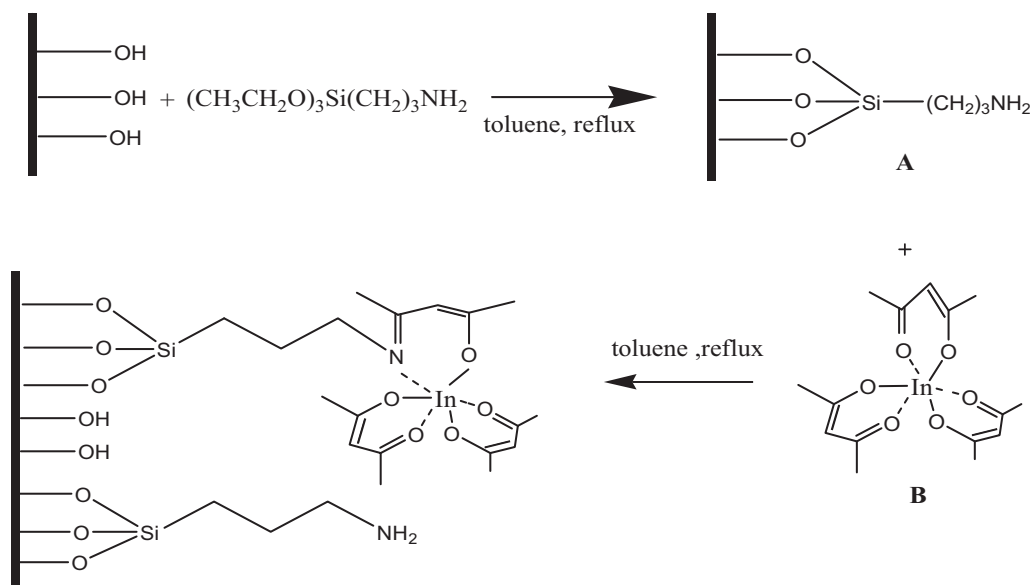
Considering the above advantages, In(acac)₃ complex has been immobilized on silica gel and used as an efficient catalyst in the synthesis of oxindoles in water. Organic reactions in water without the use of harmful organic solvents are becoming of great interest in recent years, because water is an easily available, economical, and environmentally benign solvent [15]. The 3,3-diaryloxindoles have been shown to possess a wide range of biological activities such as antibacterial, antiprotozoal and anti-inflammatory behaviour [16]. In general, these are prepared by acid-catalyzed condensation of arenes with isatin [17,18], however, there are only a few methods reported in literature for the synthesis of this class of compounds from the condensation of isatin with heteroaromatics, such as indoles [19–23], to prepare diindolyl isatin analogues. Therefore, herein we report the synthesis of 3,3-di(heteroaryl)oxindoles in aqueous-acetonitrile from various indoles and isatins using In(acac)₃-APSG as a catalyst.

2. Experimental

2.1. Materials and apparatus

Indium (III) chloride (Aldrich), 3-aminopropyltriethoxy silane (Fluka), silica gel (Qualigens) were commercially obtained and used as such in this study. Starting materials and reagents used in the

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Scheme 1. Synthesis of covalently anchored indium complex onto silica.

reactions were obtained commercially from Alfa Aesar and Spectrochem Pvt. Ltd. and used without purification. Solvents used in the present study were purified before use. The IR spectra were recorded on Perkin-Elmer Spectrum 2000 Fourier transform infrared (FT-IR) spectrometer. Thermogravimetric analysis (TGA) was carried out on a Dupont (Wilmington, Delaware, USA) 2100 thermal analyser. Surface area analysis was carried out at 77 K by Model 2010, Micromeritics, USA. Elemental analysis was performed on an Elementar Analysensysteme GmbH VarioEL V3.00. ^{13}C -CPMAS spectra were recorded on a Bruker DSX-300 NMR spectrometer at 75.47 MHz. The content of indium in the heterogenized catalyst was determined by an ICP-MS Agilent 75003 model number G3272A. ^{13}C NMR spectra were recorded on model number 400 Bruker Ultra shield at 400 MHz and ^1H NMR spectra for the products were recorded on Bruker 300 MHz instrument using TMS as internal standard. Chemical shifts (δ) are reported relative to TMS. Melting points were recorded on a Buchi R-535 apparatus and are uncorrected. The electrospray ionisation mass spectra (ESI-MS) were recorded on a Waters Micromass LCT LC/MS (Waters Corporation, Milford, MA).

2.2. Preparation of catalyst

2.2.1. Synthesis of aminopropyl silica gel (APSG), A

Silica gel was boiled with 5 N HCl for 8 h, filtered, washed with water until free from acid, dried at 110 °C for 12 h. 5 g of activated silica gel was suspended in 20 ml of 10% (v/v) 3-aminopropyltriethoxy silane in dry toluene (Scheme 1). The mixture was refluxed for 12 h in nitrogen atmosphere with constant stirring. The resulting aminopropyl silica gel (APSG) was filtered, washed consecutively with toluene, ethanol and acetone and heated at 75 °C for 10 h in vacuum oven.

2.2.2. Synthesis of indium(III) acetylacetonate complex, B

The synthesis of indium(III) acetylacetonate complex from indium(III) chloride was carried out following the method of Kozacik et al. [24]. The complex formation was confirmed by ^1H NMR, ^{13}C NMR, IR, elemental analysis and melting point. The results have also been compared with the literature values.

Melting point [24]: 187 °C. ^1H NMR [25] (CDCl_3 , 300 MHz): δ (ppm) 2.01 (s, 6H), 5.39 (s, 1H). ^{13}C NMR [26] (400 MHz): δ (ppm) 28.30, 29.69, 100.43, 101.01, 191.19, 195.26. IR (KBr cm^{-1})

1575 (C=O), 1526 (C=C), 1372 (CH_3). Elemental analysis: $\text{C}_{15}\text{H}_{21}\text{InO}_6$: C, 43.71; H, 5.14; N, 0.0. Found: C, 44.09; H, 5.14; N, 0.0.

2.2.3. Reaction of APSG with $\text{In}(\text{acac})_3$

A mixture of APSG (5 g) and $\text{In}(\text{acac})_3$ (0.75 mmol) solution in toluene was refluxed for 16 h. After that, the material was filtered, washed with ethanol and dried overnight in vacuum oven at 110 °C (Scheme 1).

2.3. Catalytic activity tests

A mixture of indole (1 mmol), isatin (0.5 mmol), catalyst (10 wt% w.r.t indole) and 5 ml water:acetonitrile (4:1) in a 20 ml flask was stirred at room temperature. After completion of the reaction (monitored by TLC, ethyl acetate:petroleum ether, 1:1), the product was filtered, washed with water and dissolved in 2 ml of acetone to

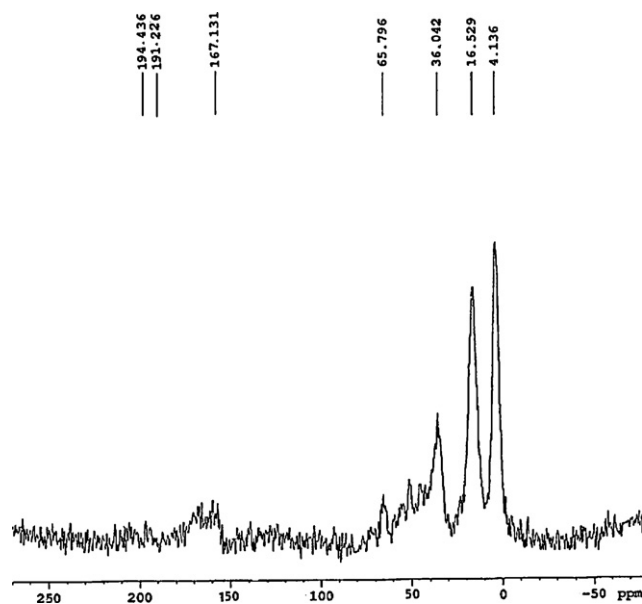


Fig. 1. ^{13}C NMR spectrum of $\text{In}(\text{acac})_3$ -APSG.

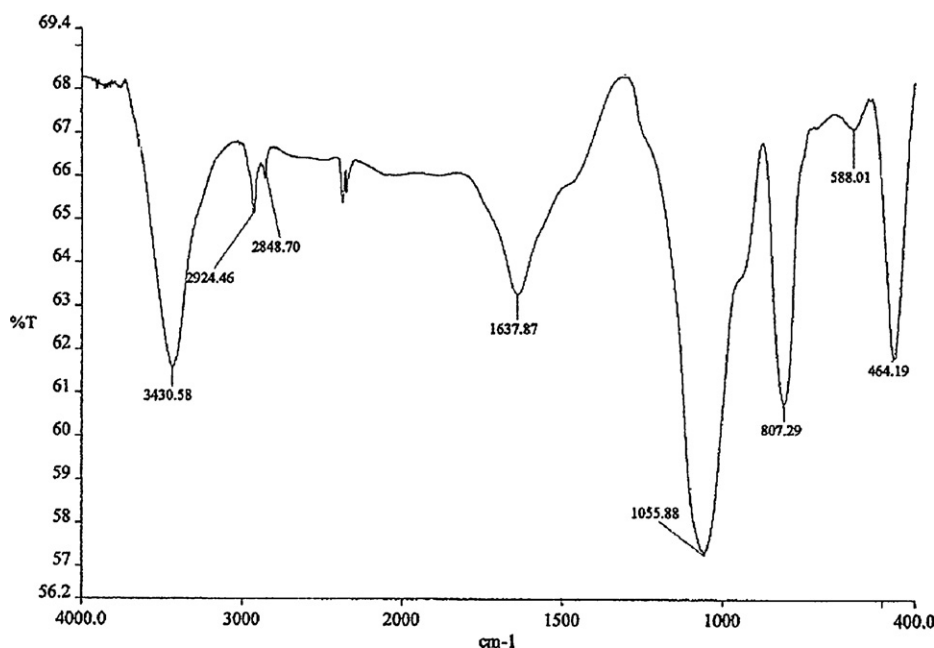


Fig. 2. FT-IR spectra of $\text{In}(\text{acac})_3\text{-APSG}$.

separate the catalyst that can be regenerated after drying at 110°C in vacuum oven overnight. The product obtained was recrystallized from ethanol to afford pure product. All products were characterized by using NMR, IR and melting points and compared with literature data [20,23]. The new compounds (entries 8 and 9) were also characterized by mass spectroscopy.

3. Results and discussion

3.1. Catalyst characterization

The three signals at 9.3, 22.3 and 42.9 ppm observed in the ^{13}C -CPMAS NMR spectrum of APSG due to $-\text{Si}-\text{CH}_2-$, $-\text{CH}_2-$ and $-\text{N}-\text{CH}_2-$ groups, respectively, authenticate the synthesis of APSG. Moreover, the covalent binding of $\text{In}(\text{acac})_3$ complex with APSG has been proved by the shifting of $-\text{N}-\text{CH}_2-$ peak to 65.6 ppm. Although other peaks are not prominent, they could be assigned to $-\text{C}=\text{O}$ (194.4 ppm), $-\text{C}-\text{O}$ (191.2 ppm), $-\text{C}=\text{N}$ (167.1 ppm), $-\text{CH}$ (97.6 ppm), $-\text{CH}_3$ (27.4 ppm, submerged into the aminopropyl peaks) (Fig. 1) [26].

Fig. 2 shows the spectra of $\text{In}(\text{acac})_3\text{-APSG}$. The spectrum of $\text{In}(\text{acac})_3$ exhibits well defined bands at about 1575 and 1526 cm^{-1} due to $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{C})$, which are slightly coupled, and at about 1372 cm^{-1} due to $\delta(\text{CH}_3)$ (where δ is in-plane bending mode) [27–29]. The spectra of the silica gel and of the modified support (see Supplementary Material) are dominated by strong bands characteristic of the support matrix. These bands are due to surface

hydroxyl groups, in the range of $3770\text{--}3300\text{ cm}^{-1}$, and to lattice vibrations, in the range of $1300\text{--}750\text{ cm}^{-1}$. Two strong bands are present at about 1094 and 797 cm^{-1} , which can be assigned to $\nu_{\text{as}}(\text{Si}-\text{O}-\text{Si})$ and $\nu_{\text{s}}(\text{Si}-\text{O}-\text{Si})$, respectively. No significant changes are observed in the silica gel structure sensitive vibrations, after its modification, which is an indication that its framework remained unchanged. The spectrum of APSG (b) exhibits an additional band at about 2924 cm^{-1} due to the aliphatic ($-\text{CH}_2$) stretching of the propyl chain of the silylating agent [30–32], thus suggesting that the silica gel surface was functionalized with the linking agent. After the Schiff condensation reaction, the characteristic band of the imine group ($\text{C}=\text{N}$), appears in the spectrum of $\text{In}(\text{acac})_3\text{-APSG}$ at 1637 cm^{-1} [33] slightly shifted from a matrix band. Another band also arises at about 1430 cm^{-1} assignable to the vibration of the acetylacetonate ring [34].

A good dispersion of active species over a high area support material is generally desirable for good catalytic activity. An incorporation of the organic groups into the silica matrix block the access of nitrogen gas molecules thereby reducing the surface area. Hence, as expected, the BET surface area strongly decreased after grafting [35], according to the sequence $\text{SG} > \text{APSG} > \text{In}(\text{acac})_3\text{-APSG}$. The reduction in surface area in this sequence confirms the functionalization of silica gel with 3-aminopropyltriethoxy silane to give APSG, and its modification with $\text{In}(\text{acac})_3$ to yield a catalyst. The BET surface area of silica gel (SG), aminopropylsilica gel (APSG) and catalyst $\text{In}(\text{acac})_3\text{-APSG}$ were measured and are represented in Table 1.

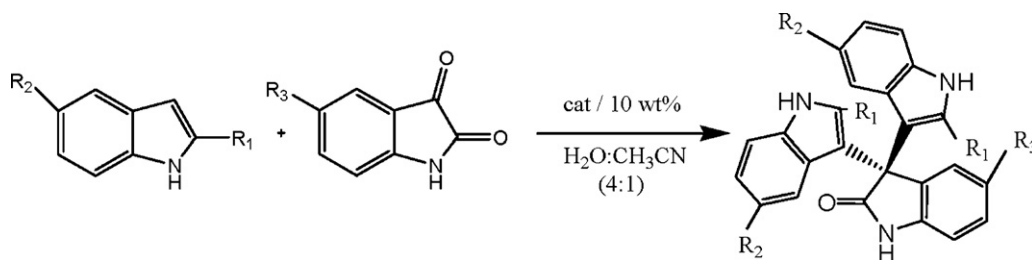
Table 1

Physico-chemical parameters of silica gel (SG), aminopropyl silica gel (APSG) and catalyst.

Material	Elemental analysis			BET surface area ($\text{m}^2\text{ g}^{-1}$)	Thermal analysis	
	%C	%H	%N		Δm^a (%)	ΔT^b ($^\circ\text{C}$)
SG	–	–	–	235.67	–	–
APSG	5.281	1.269	2.046	151.91	3.3	0–180
$\text{In}(\text{acac})_3\text{-APSG}$	7.868	1.349	1.812	138.96	8.57	180–600
					1.6	0–180
					10.7	180–600

^a Change in mass of material.

^b Change in temperature.



Scheme 2. Synthesis of oxindoles catalyzed by covalently anchored $\text{In}(\text{acac})_3$ complex onto silica.

The quantitative estimation of organic functional group covalently anchored onto the surface of silica gel was performed with elemental, and thermogravimetric analyses. The results obtained from these two techniques have also been compared to authenticate the synthesis of APSG and catalyst.

Elemental analysis was carried out for APSG and $\text{In}(\text{acac})_3$ -APSG. The nitrogen content of APSG was 2.046%. According to this value, the amount of the ligand, which was attached to silica gel, was 1.46 mmol/g of support. The metal loading of $\text{In}(\text{acac})_3$ -APSG, which was determined by inductively coupled plasma mass spectrometry technique (ICP-MS), was obtained to be 0.149 mmol/g. This value shows that catalyst has free $-\text{NH}_2$ groups as well. The observed carbon and nitrogen contents of APSG shows C/N ratio to be ~ 3 thereby confirming the incorporation of 3-aminopropyltriethoxy ligand into the silica matrix (Table 1).

Thermogravimetric curves showed two distinct stages of decomposition. The one between 30 and 180 °C was related to adsorbed water and other one between 180 and 600 °C was assigned to decomposition of organic matter and water from silanol groups condensation. The detailed thermogravimetric data are presented in Table 1. The weight loss due to the decomposition of organic matter gives rise to the grafting capacity of 1.47 mmol g^{-1} which is in good agreement with the results of elemental analysis. TG curve of $\text{In}(\text{acac})_3$ -APSG shows that water loss is 1.6%, whereas the organic degradation ends at 600 °C (10.8%). The elemental analysis of $\text{In}(\text{acac})_3$ -APSG (C=7.868 and N=1.812%) is close to the weight loss of TGA. Consequently, the weight loss due to $\text{In}(\text{acac})_3$ is calculated from elemental analysis to be only 11.02% enabling a theoretical capacity of 0.143 mmol g^{-1} of $\text{In}(\text{acac})_3$ -APSG.

3.2. Catalytic activity of $\text{In}(\text{acac})_3$ -APSG in synthesis of oxindoles

The model reaction of indole (1.0 mmol) and isatin (0.5 mmol) in water was tested in the presence of catalytic amounts of var-

Table 3
Synthesis of oxindoles using $\text{In}(\text{acac})_3$ -APSG as catalyst at room temperature.

Entry ^a	R ¹	R ²	R ³	Time (h)	Yield (%) ^b	m.p. (°C)	Lit. m.p. (°C)
1	H	H	H	2.5	92, 90, 89, 88, 88, 87 ^c	312	311–313 [32]
2	H	H	Br	4.0	89	310–312	310–311 [32]
3	H	H	NO ₂	4.0	88	296–298	298–299 [32]
4	Me	H	H	3.0	91	300–301	300–301 [32]
5	Me	H	Br	3.5	90	180–182	180–182 [29]
6	H	Br	H	5.0	87	320–321	318–319 [29]
7	H	Br	Br	5.5	88	328–329	329–330 [29]
8	H	OMe	H	3.0	93	292–294	–
9	H	NO ₂	H	6.0	81	328–330	–
10	H	Br	NO ₂	12.0	0	–	–
11	H	NO ₂	Br	12.0	0	–	–
12	H	NO ₂	NO ₂	12.0	0	–	–

^a Structure of the products confirmed by ¹H NMR, IR, and melting points and compared with authentic samples prepared according to the known procedure whereas entries 8 and 9 were also confirmed by LC-MS.

^b Yields of crude isolated products based on indole.

^c The same catalyst was used for each of the six runs.

Table 2
Effect of temperature and solvents on the product yield.

S. no.	Solvent	Time (h)	Yield (%) ^a
1	Toluene	12.0	–
2	Dichloromethane (DCM)	7.5	83
3	Acetonitrile	5.0	89
4	Water:acetonitrile (4:1)	3.5	92, 93 ^b

^a Yields of crude isolated products based on indole.

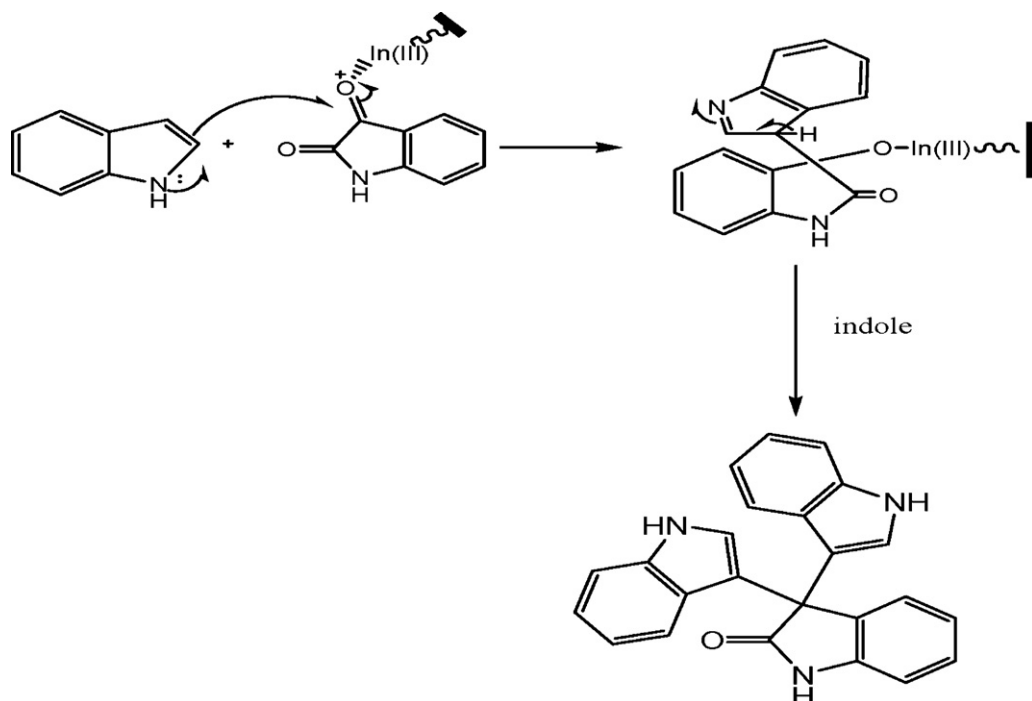
^b The same experiment when carried out at reflux.

ious metal salts (MX_3 , 2 mol%) where, M=Cr, Mn, Co, Cu, In and X=Cl, CH_3COO at room temperature. It was observed that InCl_3 was the only metal salt that catalyzed the reaction with high turnover numbers. Indium(III) acetylacetonate prepared from InCl_3 was also found to be an efficient catalyst. Therefore, we heterogenized $\text{In}(\text{acac})_3$ onto modified silica gel in order to obtain high turnover number when compared to homogeneous catalyst and also to make the catalyst recyclable.

To optimize the reaction conditions, a mixture of indole (1.0 mmol), isatin (0.5 mmol), and catalyst (10 wt% w.r.t. indole) was reacted in a 20 ml flask using 5 ml of different solvents (Table 2). It was observed that increase in the polarity of solvents increases the yield of the product though no such effect was observed for carrying out the same reaction at higher temperature.

Once the reaction conditions have been optimized, a variety of indoles and isatins were reacted in the presence of catalyst (10 wt%) and 5 ml water:acetonitrile (4:1) in a 20 ml flask at room temperature (Scheme 2). After completion of the reaction (monitored by TLC, ethyl acetate:petroleum ether, 1:1), the product was filtered, washed with water and recrystallized in ethanol to afford pure product. The results are summarized in Table 3.

Since the reaction follows electrophilic substitution reaction mechanism (Scheme 3), yield of the product reduces with the increase in the electron-withdrawing nature of the substituent on isatin. However, indoles bearing electron-donating groups found to



Scheme 3. Electrophilic substitution reaction mechanism for synthesis of oxindoles derivatives.

be more active than the ones bearing electron-withdrawing substituent. The resulting oxindoles show two signals for –NH protons in 2:1 ratio, whereas if indoles are substituted at second position, the resulting oxindole–NH protons become diastereotopic and show three signals in ^1H NMR in 1:1:1. However, no such effect could be seen when substitution is made at fifth position of indoles.

The catalyst was recovered by simple filtration and washed with acetone and air-dried. The recovered catalyst was re-used and consistent activity was noticed even after sixth cycle. To test the recyclability of a catalyst, it was filtered out from the reaction mixture after half of the reaction time. It was observed that there was no increase in the product yield; that proves the heterogeneity of our catalyst.

4. Conclusions

In conclusion, we have developed a mild, simple, cost-effective and green procedure for the synthesis of 3,3-diaryl oxindoles using re-usable covalently anchored indium(III) acetylacetonate complex onto the surface of functionalized silica gel. Moreover, the mild reaction conditions, high yield of products, ease of work-up, compatibility with various functional groups, and the reusability of catalyst, will make the present method a useful and important addition to the present methodologies for the oxindoles synthesis.

Acknowledgements

One of the authors, C. Sharma thanks the Council of Scientific & Industrial Research (CSIR), New Delhi, India, for the award of Junior and Senior research fellowships. The authors also thank Indian Institute of Science (IISc), Bangalore for performing ^{13}C NMR measurements.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2010.08.020.

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