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Recyclable silica-supported iodoarene–$RuCl_3$ bifunctional catalysts for oxidation of alcohols and alkylarenes

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ABSTRACT

Novel, efficient, and recyclable bifunctional catalysts bearing SiO_2-supported $RuCl_3$ and iodoarene moieties were developed and used for environmentally benign oxidation of alcohols or alkylarenes at the benzylic position. These reactions in the presence of oxone as stoichiometric oxidant afforded the corresponding carbonyl compounds in high yields under mild conditions and convenient work-up. Furthermore, these SiO_2-supported bifunctional catalysts can be recovered by simple filtration and directly reused.

Selective oxidation of alcohols and aromatic hydrocarbons into the corresponding carbonyl compounds is one of the most fundamental and important transformations in synthetic organic chemistry.[1,2] Environmentally benign procedures are especially important for the production of pharmaceuticals, flavors and fragrances, and agrochemicals. Thus, there is an increasing demand for oxidation process that is catalytic and uses green, economic, and efficient oxidants.

As oxidants, hypervalent iodine reagents have recently received much attention due to their low toxicity, mild reactivity, ready availability, high stability, easy handling, etc.[3,4] However, their low atom economy remains a major drawback, as stoichiometric amount of aryliodides or similar waste products is produced, which complicates isolation and purification of the products.[5,6] Therefore, the catalytic utilization of hypervalent iodine reagents, in view of economical and environmental requirements, is the most attractive strategy, and new reaction systems based on catalytic iodine(V) species and a stoichiometric oxidant have recently been developed,[4] including publications from our group.[2b,7] However, synthetic value of the iodine(V)-based catalytic cycles is limited by the reoxidation step of iodine(I) or iodine(III) to the iodine(V) species, which proceeds relatively slowly even at temperatures above 70 °C.[8] Recently, we have reported an extremely mild and efficient iodine(V)/$RuCl_3$ tandem catalytic system for the oxidation of alcohols and alkylarenes using oxone ($2KHSO_5\cdot KHSO_4\cdot K_2SO_4$) as a stoichiometric oxidant,[2b] in which ruthenium catalyst dramatically accelerates the reaction under mild conditions.

However, the homogeneously catalyzed organic reactions commonly suffer from disadvantages, such as difficult separation of the product and recovery of the catalyst. These problems can be addressed by the immobilization of homogeneous catalysts onto solid supports. Recently, silica-supported catalytic metallic species have been successfully employed in aqueous media,[9] since silica displays many advantageous properties—excellent stability (both chemical and thermal), high surface area, good accessibility, and organic groups can be robustly anchored to the surface, to provide catalytic centers.[10]

The analysis of literature data encouraged us to develop efficient bifunctional hybrid-type catalysts by immobilization of both hypervalent iodine and $RuCl_3$ onto solid silica gel supports. Hybridization of these two moieties should result in more efficient oxidation of organic substrates under mild conditions. Furthermore, the combination of both co-catalysts in one reagent should make the recovery and reuse of both hypervalent iodine and ruthenium much easier. As a part of our studies[2b,7,11] toward the development of practical and environmentally benign oxidation reactions, we herein, report the synthesis of SiO_2-supported iodoarene–$RuCl_3$ bifunctional catalysts **5** and **6** (Scheme 1), which are useful for environmentally benign oxidation of alcohols or alkylarenes in acetonitrile–water mixture at room temperature.

Our approach to the preparation of such SiO_2-supported iodoarene–$RuCl_3$ bifunctional catalysts **5** and **6** consists of building a suitable ligand structure **3** or **4** on the surface of commercial

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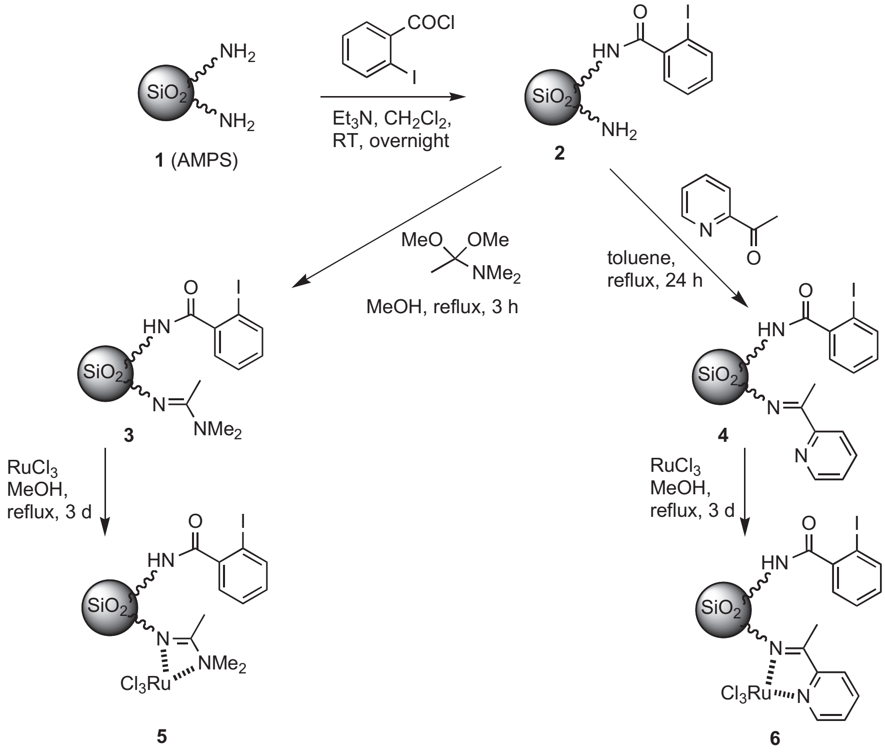


Scheme 1. Synthesis of SiO_2-supported iodoarene–$RuCl_3$ bifunctional catalysts **5** and **6**.

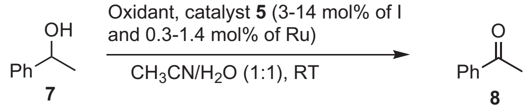
aminopropyl silica (AMPS, **1**), followed by complexation with $RuCl_3$ (Scheme 1). The synthesized catalysts **5** and **6** were characterized by FT-IR and elemental analysis. The amount of the $RuCl_3$ and iodine loaded on the surface of silica gel was determined by elemental analyses of chlorine and iodine. The loadings of iodine and ruthenium for catalyst **5** are 0.60 mmol/g and 0.06 mmol/g, respectively, and for catalyst **6** 0.62 mmol/g and 0.05 mmol/g, respectively. For comparison, the ratio of catalytic iodine to ruthenium in the previously reported tandem catalytic system PhI/$RuCl_3$ was 31:1.[2b]

To investigate catalytic activity of the new bifunctional catalysts in the oxidation of alcohols, the reaction was first optimized using 1-phenylethanol **7** as a model substrate, polymer **5** as a catalyst, and several common stoichiometric oxidants (Table 1). As expected, in the absence of catalyst **5** the oxidation of substrate **7** at room temperature proceeded extremely slowly (Table 1, entry 1) using oxone as the oxidant. The combined application of **5** and oxone (1.5–3 equiv) resulted in fast oxidation of **7** to acetophenone **8** with up to 100% conversion (Table 1, entries 2–5). The yield of product reached maximum at 15–30 mg of catalyst per 0.2 mmol of alcohol (Table 1, entries 3 and 4). Further increases in the amount of catalysts (Table 1, entry 5) resulted in a lower yield, probably due to the rapid decomposition of oxidant before oxidizing the substrate (see Ref. 2b). Other oxidants, such as MCPBA and peracetic acid showed slightly lower reactivity and lack of selectivity as compared to oxone (Table 1, entries 6 and 7). Previously, oxone has been employed as environmentally safe co-oxidant for hypervalent iodine-catalyzed oxidations;[8] moreover, oxone is commercially available and an inexpensive reagent.[12] The optimized reaction required at least 3 mol equiv of oxone and 15 mg (5 mol % of I and 0.5 mol % of Ru) of catalyst **5** for the oxidation of alcohols.

Various alcohols **9** were smoothly oxidized to corresponding products **10** or **11** under optimized reaction conditions in excellent yields at room temperature (Table 2). Similar to the high-temperature ArI/oxone procedure,[8a] secondary benzylic alcohols and alicyclic alcohols were converted to the respective ketones **10** (Table 2, entries 5–13). However, depending on the substituent on the benzene ring, different types of products were obtained in the reactions of primary benzylic alcohols; for example, the oxidation of benzyl alcohol afforded benzoic acid (Table 2, entries 1 and 2), while 4-nitrobenzyl alcohol gave exclusively 4-nitrobenzaldehyde (Table 2, entries 3 and 4) in excellent yields. These results differed from the results reported by Ishihara and co-workers[8a] and by our group.[2b] Both catalysts **5** and **6** showed similar catalytic activity in the oxidation of alcohols.

Selective oxidation of the benzylic C–H bonds is of particular interest for organic chemists. Recently, Vinod and co-workers reported the oxidation of benzylic C–H bonds performed under

Table 1
Effect of oxidant and catalyst **5** on the oxidation of 1-phenylethanol[a]



Entry	Cat. **5** (mg)	Oxidant (equiv)	Time (h)	Conversion[b] (%)	Yield[c] (%)
1	None	Oxone (3)	24	0	0
2	10	Oxone (1.5)	12	86	85
3	15	Oxone (3)	2	100	98
4	30	Oxone (3)	2	100	98
5	45	Oxone (3)	4.5	92	92
6	10	MCPBA (1.5)	3.5	87	87
7	10	AcOOH (1.5)	4	86	47[d]

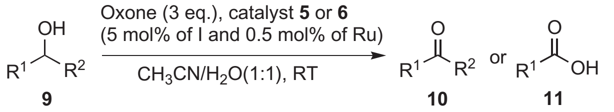
[a] All reactions were performed at room temperature using 1-phenylethanol (0.2 mmol), catalyst **5** (10–45 mg; 0.006–0.027 mmol of I and 0.0006–0.0027 mmol Ru), and oxidant (1.5–3.0 equiv) in MeCN/H_2O (1:1 v/v) unless otherwise noted.

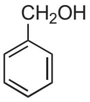
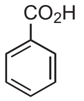
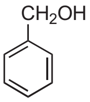
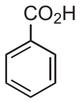
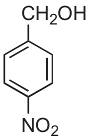
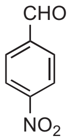
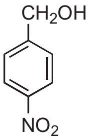
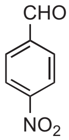
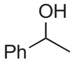
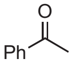
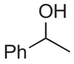
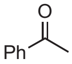
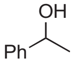
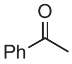
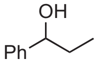
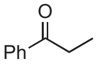
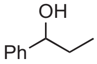
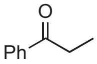
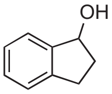
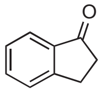
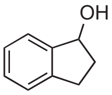
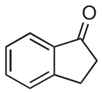
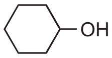
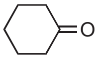
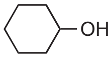
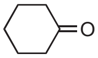
[b] Based on GC–MS analysis.

[c] Yields of isolated products.

[d] In addition to product **8**, 1-acetoxy-1-phenylethane was isolated in 38% yield.

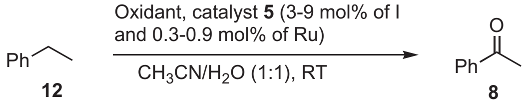
Table 2
Oxidation of alcohols catalyzed by SiO_2-supported bifunctional catalysts **5** and **6**[a]



Entry	Catalyst	Alcohol	Product	Time (h)	Yield[b] (%)
1	**5**			2	88
2	**6**			2.5	90
3	**5**			9.5	96
4	**6**			12	94
5	**5**			2	98
6	**6**			1.5	97
7	**5**[c]			1.5	86
8	**5**			5	79
9	**6**			1	96
10	**5**			3.5	92
11	**6**			2.5	88
12	**5**			1.5	92
13	**6**			1.5	81

[a] All reactions were performed at room temperature using alcohol (0.2 mmol), catalyst **5** or **6** (15 mg, 0.009 mmol of I and 0.0009 mmol Ru), and oxone (0.6 mmol) in $MeCN/H_2O$ (1:1 v/v) unless otherwise noted.
[b] Yields of isolated products.
[c] Recycled catalyst **5** was used.

Table 3
Effect of oxidant and catalyst **5** on the oxidation of ethylbenzene[a]



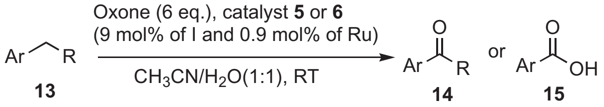
Entry	Cat. **5** (mg)	Oxidant (equiv)	Time (h)	Conversion[b] (%)	Yield[c] (%)
1	None	Oxone (3.0)	24	0	0
2	10	Oxone (1.5)	24	17	16
3	30	Oxone (6.0)	12	99	98
4	10	MCPBA (3.0)	24	0.18	0
5	10	AcOOH (3.0)	24	0	0

[a] All reactions were performed at room temperature using ethylbenzene (0.2 mmol), catalyst **5** (10–30 mg; 0.006–0.018 mmol of I and 0.0006–0.0018 mmol Ru), and oxidant (1.5–6.0 equiv) in $MeCN/H_2O$ (1:1 v/v) unless otherwise noted.
[b] Based on GC–MS analysis.
[c] Yields of isolated products.

catalytic conditions by IBX formed in situ using oxone as a terminal oxidant at 70–80 °C for 8–48 h.[2a] Our group has also reported the oxidation of C–H bonds by using the $ArI/RuCl_3$ tandem catalytic system at room temperature under mild conditions.[2b] We investigated the catalyzed oxidation of C–H bonds using the SiO_2-supported iodoarene–$RuCl_3$ bifunctional catalyst **5**. The reaction was optimized using ethylbenzene **12** as a model substrate (Table 3). As expected, in the absence of catalyst **5** and in the presence of oxone, or in the presence of catalyst **5** and MCPBA or peracetic acid the oxidation of substrate **12** at room temperature did not occur or did not show any measurable conversion after 24 h (Table 3, entries 1, 4, and 5). The reaction also proceeded very slowly when smaller quantities of oxone were used (Table 3, entry 2). The optimized reaction conditions led to 99% conversion of substrate **12** to product **8** and required 6.0 mol equiv of oxone over 12 h and the use of 30 mg (9 mol % of I and 0.9 mol % of Ru) catalyst **5** (Table 3, entry 3).

Results of the oxidation of several other aromatic hydrocarbons under optimized catalytic conditions using catalyst **5** or **6** were summarized in Table 4. In general, moderate to high isolated yields of aromatic ketones were obtained in these oxidations under very mild reaction conditions (Table 4, entries 1–10). Compared with the high-temperature IBX/oxone procedure,[2a] our protocol was much more selective and generally did not afford products of C–C bond cleavage, similarly to the results reported previously for the $ArI/RuCl_3$ tandem catalytic system.[2b] Interestingly, toluene was oxidized in 2 h with the major product being benzaldehyde; however, with the reaction time extended to 24 h, benzaldehyde is almost totally converted to benzoic acid (Table 4, entries 11 and 12). Moreover, catalyst **6** showed noticeably higher catalytic reactivity in the oxidation of anthrancene and indane compared to catalyst **5** (Table 4, entries 6–9). Recycled catalyst **6** showed slightly lower activity compared to the fresh catalyst (Table 4,

Table 4
Oxidation of aromatic hydrocarbons catalyzed by SiO_2-supported bifunctional catalysts **5** and **6**[a]



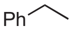
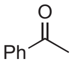
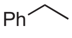
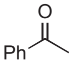
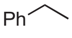
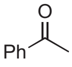
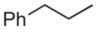
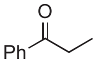
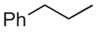
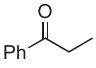
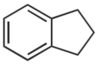
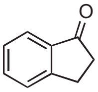
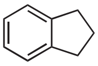
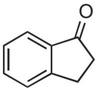
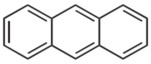
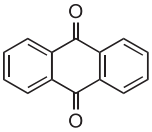
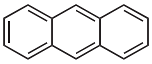
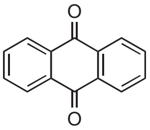
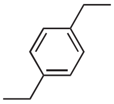
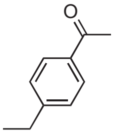
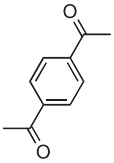
Entry	Catalyst	Substrate	Product	Time (h)	Yield[b] (%)
1	**5**			12	98
2	**6**			12	94
3	**6**[c]			12	71
4	**5**			24	59
5	**6**			12	58

Table 4 (*continued*)

Entry	Catalyst	Substrate	Product	Time (h)	Yield[b] (%)
6	**5**			24	68
7	**6**			12	92
8	**5**			24	25
9	**6**			6	83
10	**6**			12	77
					15
11	**5**	$PhCH_3$	$PhCO_2H$ PhCHO	24	85 [d]
12	**6**	$PhCH_3$	$PhCO_2H$ PhCHO	24	80 [d]

[a] All reactions were performed at room temperature using alkylarene (0.2 mmol), catalyst **5** or **6** (30 mg, 0.018 mmol of I and 0.0018 mmol of Ru), and oxone (1.2 mmol) in $MeCN/H_2O$ (1:1 v/v) unless otherwise noted.

[b] Yields of isolated products.

[c] Recycled catalyst **6** was used.

[d] Preparative yield of benzoic acid; benzaldehyde was present as a minor product (under 10% as estimated by ^1H NMR of reaction mixture).

entry 3), which was similar to the activity of recovered catalyst **5** (Table 2, entry 7).

In summary, we designed and synthesized novel bifunctional SiO_2-supported iodoarene–$RuCl_3$ catalysts bearing two catalytic sites, the iodoarene and $RuCl_3$ moieties. These catalysts were demonstrated to be useful for the efficient and environmentally benign oxidation of alcohols and aromatic hydrocarbons to corresponding carbonyl compounds using oxone as a stoichiometric oxidant. Due to the mild reaction conditions, our protocol is highly selective and generally does not afford products of the C–C bond cleavage. Moreover, these bifunctional catalysts can be recovered by simple filtration and directly reused.

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Supplementary data

Supplementary data (experimental procedures and ^1H and ^{13}C NMR spectra for representative products) associated with this Letter can be found, in the online version, at doi:10.1016/j.tetlet.2011.08.097.

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