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# Novel rhenium(i) catalysts for the isomerization of propargylic alcohols into $\alpha,\beta$ -unsaturated carbonyl compounds: an unprecedented recyclable catalytic system in ionic liquids<sup>†</sup>

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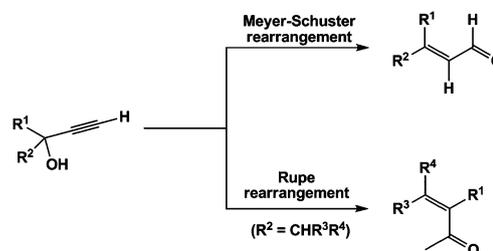
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Carbonyl rhenium(i) complexes are efficient catalysts for the regioselective isomerization of terminal propargylic alcohols into  $\alpha,\beta$ -unsaturated aldehydes or ketones which can be used as an unprecedented recyclable catalytic system (up to 10 consecutive runs) in the ionic liquid [BMIM][PF<sub>6</sub>].

Rhenium(i) catalyzed reactions have focused a growing attention during the last few years,<sup>1</sup> providing unique modes of reactivity<sup>1–3</sup> and disclosing performances which can be competitive with efficient procedures attained by other transition metal catalysts. Despite that rhenium(i) and ruthenium(ii) are isoelectronic d<sup>6</sup> species<sup>4</sup> and feature parallel coordination chemistry, they display a different organometallic chemistry. Although these features may open up new efficient synthetic methodologies, the number of rhenium(i) catalyzed reactions still remains much more limited as compared with conventional ruthenium(ii) based catalysts.

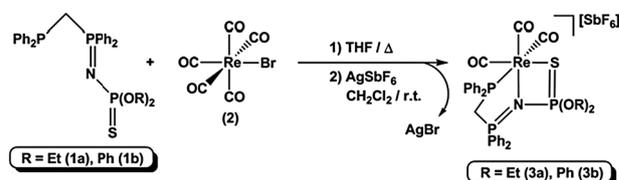
Following our interest in ruthenium(ii) catalyzed reactions with atom-economy,<sup>5</sup> we were interested to find out whether rhenium(i) derivatives can improve the catalytic performances. Recently, we have described the synthesis of ( $\eta^6$ -arene)-ruthenium(ii) complexes containing the hemilabile heterotridentate iminophosphorane-phosphane ligands Ph<sub>2</sub>PCH<sub>2</sub>P{=NP(=S)(OR)<sub>2</sub>}Ph<sub>2</sub>.<sup>6</sup> Encouraged by their catalytic activity<sup>6</sup> we set up the synthesis of analogous rhenium(i) complexes. Herein, we report a new type of cationic rhenium(i) complexes [Re( $\kappa^3$ -P,N,S-Ph<sub>2</sub>PCH<sub>2</sub>P{=NP(=S)(OR)<sub>2</sub>}Ph<sub>2</sub>)(CO)<sub>3</sub>][SbF<sub>6</sub>] (**3a,b**) which are efficient catalysts for the regio and stereoselective isomerisation of propargylic alcohols into  $\alpha,\beta$ -unsaturated aldehydes (Meyer–Schuster (M–S) rearrangement) or ketones (Rupe rearrangement)<sup>7</sup> (see Scheme 1). It is important to note that: (i) these are the first rhenium catalysts which are active in both M–S and Rupe rearrangements,<sup>8</sup> (ii) a higher catalytic efficiency than that observed for ruthenium(ii)



**Scheme 1** The Meyer–Schuster and Rupe rearrangements of terminal propargylic alcohols.

catalysts is achieved and no addition of co-catalysts (TFA) is needed,<sup>5a</sup> and (iii) the catalytic isomerization also proceeds efficiently in ionic liquids as reaction media allowing for the first time the catalyst recycling (Scheme 2).

The rhenium(i) complexes **3a–b**<sup>9</sup> have been readily prepared by the treatment of [ReBr(CO)<sub>5</sub>] (**2**) with an equimolecular amount of **1a–b**, in refluxing THF, followed by bromine extraction with AgSbF<sub>6</sub>.



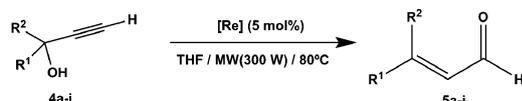
**Scheme 2** Coordination of the iminophosphorane-phosphane ligands Ph<sub>2</sub>PCH<sub>2</sub>P{=NP(=S)(OR)<sub>2</sub>}Ph<sub>2</sub> **1a,b** to the Re(i) precursor [ReBr(CO)<sub>5</sub>].

Conductance measurements for **3a,b** in acetone show that these complexes are 1:1 electrolytes (110–120  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ). Complexes **3a,b** (93–99% yields) were fully characterized by IR and <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy (see ESI<sup>†</sup>). In particular, the  $\kappa^3$ -P,N,S-coordination of ligands **1a,b** to rhenium is clearly reflected in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **3a,b** by: (i) an appreciable downfield shift of both the PPh<sub>2</sub> and Ph<sub>2</sub>P=N signals, and (ii) a slight high-field shifting of the (RO)<sub>2</sub>P=S resonances (see ESI<sup>†</sup> for further data).<sup>10</sup> Moreover, the formation of the cationic complexes **3a,b** was unambiguously confirmed by a single-crystal X-ray diffraction study of complex **3a** (see ESI<sup>†</sup>).

The catalytic activity of complexes **3a,b** was firstly evaluated by using the isomerization of the commercially available

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<sup>†</sup> Electronic supplementary information (ESI) available: For the synthesis of compounds **3a–b**, catalytic procedure and crystallographic data for **3a**. CCDC 806226. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc10768b

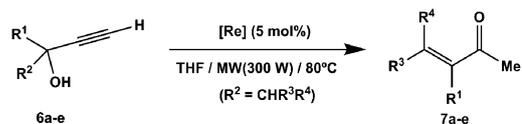
**Table 1** Isomerization of propargylic alcohols **4a–i** into  $\alpha,\beta$ -unsaturated aldehydes **5a–i** catalyzed by complex **3b**<sup>a</sup>

Entry	R <sup>1</sup>	R <sup>2</sup>	Product	Time/ min	GC yield [%], isolated (%)
1	Ph	Ph	<b>5a</b>	5	99(91)
2	<i>p</i> -F(C <sub>6</sub> H <sub>4</sub> )	<i>p</i> -F(C <sub>6</sub> H <sub>4</sub> )	<b>5b</b>	15	97(94)
3	<i>p</i> -Cl(C <sub>6</sub> H <sub>4</sub> )	<i>p</i> -Cl(C <sub>6</sub> H <sub>4</sub> )	<b>5c</b>	60	98(93)
4	<i>p</i> -MeO(C <sub>6</sub> H <sub>4</sub> )	<i>p</i> -MeO(C <sub>6</sub> H <sub>4</sub> )	<b>5d</b>	10	99(94)
5	<i>p</i> -Me(C <sub>6</sub> H <sub>4</sub> )	<i>p</i> -Me(C <sub>6</sub> H <sub>4</sub> )	<b>5e</b>	5	97(94)
6	Ph	H	<b>5f</b>	5	96(92)
7	Naphthyl	H	<b>5g</b>	90	97(91)
8	<i>p</i> -Cl(C <sub>6</sub> H <sub>4</sub> )	H	<b>5h</b>	30	99(85)
9	<i>p</i> -MeO(C <sub>6</sub> H <sub>4</sub> )	H	<b>5i</b>	15	97(93)

<sup>a</sup> Reactions were performed under a N<sub>2</sub> atmosphere in a CEM Discover<sup>®</sup> S-Class microwave synthesizer at 80 °C through moderation of the initial power (300 MW). 1 mmol of the corresponding alkyne was used.

1,1-diphenyl-2-propyn-1-ol (**4a**) into 3,3-diphenylpropenal (**5a**) as a model reaction (see Table 1). Thus, in a typical experiment, the Re(I) precursor (5 mol% of Re) was added to a 1 M solution of the propargylic alcohol **4a** in THF, using as heating source microwave irradiation at 80 °C, the course of the reaction being monitored by gas chromatography.<sup>11</sup> Both cationic complexes were found to be active and selective catalysts in the isomerization process providing the enal **5a** as the unique reaction product. The best result was obtained for complex **3b**, which led to the enal **5a** in quantitative yield (99%) after only 5 minutes of reaction vs. 10 min of reaction for complex **3a**.<sup>12</sup>

As observed for 1,1-diphenyl-2-propyn-1-ol (entry 1, Table 1), complex **3b** was also found to be an efficient catalyst for the selective isomerisation of other tertiary (entries 2–5) and secondary (entries 6–9) propargylic alcohols to the corresponding enals (stereoselective *E* enals were obtained for the latter).<sup>13</sup> Influence of the electronic properties of the aryl rings on the reaction rates was observed. Thus, alkynols with electron-withdrawing groups showed less reactivity (entries 2 and 3) as compared to the substrates with electron-donating groups (entries 4 and 5).<sup>14</sup> No transformation was observed when internal propargylic alcohols such as PhC≡CC(OH)Ph<sub>2</sub> or MeC≡CCH<sub>2</sub>(OH) were used as substrates.<sup>15</sup> The catalytic activity of complex **3b** was then tested in the isomerisation of propargylic alcohols which contain a C–H bond in the  $\beta$ -position with respect to the alcohol group (**6a–e**). Gratifyingly, the process proceeds in a different way, giving rise to the selective formation of  $\alpha,\beta$ -unsaturated methyl ketones (**7a–e**) in high yield via a formal Rupe-type rearrangement of the alkynol (see Table 2). This catalytic transformation can be also applied successfully to more elaborated substrates such as the hormonal steroid mestranol (**6d**, entry 4) and ethisterone (**6e**, entry 5). The corresponding enones **7d,e** which are important building blocks in the chemistry of steroids have been obtained selectively in a pure form with excellent yields (94–99%). As far as we are aware, complex **3b** represents the first example of a rhenium catalyst active in the Rupe-type rearrangement of propargylic alcohols.

**Table 2** Isomerization of propargylic alcohols **6a–e** into  $\alpha,\beta$ -unsaturated ketones **7a–e** catalyzed by complex **3b**<sup>a</sup>

Entry	Substrate	Product	Time/ min	GC yield [%], isolated (%)
1		<b>7a</b>	75	97(93)
2		<b>7b</b>	120	98(91)
3		<b>7c</b>	165	99(94)
4		<b>7d</b>	75	94(91)
5		<b>7e</b>	275	99(91)

<sup>a</sup> Reactions were performed under a N<sub>2</sub> atmosphere in a CEM Discover<sup>®</sup> S-Class microwave synthesizer at 80 °C through moderation of the initial power (300 MW). 1 mmol of the corresponding alkyne was used.

Given that, as far as we know, no catalyst recovery has been reported to date for MS and Rupe rearrangements we decided to explore the recycling of catalyst **3b** by using ionic liquids (IL) as solvent.<sup>16</sup> The reaction rate was found to be dependent on the IL nature, the highest rate being attained by using [BMIM][PF<sub>6</sub>] (BMIM = 1-butyl-3-methylimidazolium) as solvent.<sup>17</sup> It is important to note that the reaction is selective since no side products could be detected by means of GC or NMR spectra.<sup>18</sup> Under the optimized reaction conditions (see Table 3),<sup>19</sup> we have found that the catalytic system remains active (97–99% yield) after recycling up to 10 times. As expected, a gradual decreasing of the activity is found after each recycling, 10–40 min for the first four cycles (entries 1–4) while two hours of heating is required after the fifth cycle.

**Table 3** Re(I)-catalyzed (**3b**) Meyer–Schuster isomerization of **4a** into **5a** using [BMIM][PF<sub>6</sub>] as solvent<sup>a</sup>

Cycle	<i>t</i> /min	Yield <sup>b</sup>	TON	Cycle	<i>t</i> /h	Yield <sup>b</sup>	TON <sup>c</sup>
1	10	99	20	6	2	97	118
2	20	99	40	7	3.3	97	138
3	30	99	60	8	6.5	99	158
4	40	99	80	9	8	99	178
5	120	99	99	10	10	99	200

<sup>a</sup> Reactions were performed under a N<sub>2</sub> atmosphere at 80 °C using 1 mmol of the alkynol **4a** in 1 g of [BMIM][PF<sub>6</sub>] with 5 mol% of catalyst **3b**. <sup>b</sup> Determined by GC. <sup>c</sup> Cumulative TON values (turnover number = (mol product/mol Re)).

The catalytic activity of **3b** using [BMIM][PF<sub>6</sub>] as solvent was then tested in the Rupe-type rearrangement of **6b** (1-ethynylcyclohexanol) into the  $\alpha,\beta$ -unsaturated methyl ketone **7b**. A higher temperature (130 °C) is required with respect to the Meyer–Schuster rearrangement (80 °C) to attain quantitative transformations. Moreover, the catalyst **3b** could only be recycled up to 4 times [1st cycle: 1.5 h (99%); 2nd cycle 3.5 h (99%); 3rd cycle 5 h (98%); 4th cycle 20 h (97%)], with reaction times between 90 minutes to 20 hours.

In summary, in this work, we have shown that the cationic Re(i) complex [Re( $\kappa^3$ -P,N,S-Ph<sub>2</sub>PCH<sub>2</sub>P{=NP(=S)(OPh)<sub>2</sub>}Ph<sub>2</sub>)-(CO)<sub>3</sub>][SbF<sub>6</sub>] (**3b**) is a highly efficient catalyst for the isomerization of terminal propargylic alcohols into  $\alpha,\beta$ -unsaturated carbonyl compounds, which can be obtained in excellent yield and in a time-scale reaction of minutes. This catalyst has also proven to promote chemoselective transformations producing either enals (Meyer–Schuster rearrangement) or enones (Rupe rearrangement) depending on the nature of the propargylic alcohol. As far as we are aware, complex **3b** is the first example of a rhenium catalyst active in the Rupe-type rearrangement of propargylic alcohols. Moreover, **3b** is also an efficient catalyst in the ionic liquid [BMIM][PF<sub>6</sub>]. The use of this environmentally friendly solvent allows the catalyst recovery disclosing an unprecedented appealing synthetic approach for the chemoselective isomerisation of propargylic alcohols with practical utility.<sup>20</sup> Mechanistic studies and further synthetic applications of this catalytic system as an appealing alternative to the widely used ruthenium(II) catalysts are presently underway.

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- These data are in accordance with those reported previously in the  $\kappa^3$ -P,N,S-coordination of **1a,b** to Ru(II) fragments see ref. 6.
- A parameter study of the catalytic activity of complex **3b** with substrate **4a** using different solvents, heating sources and acid co-catalyst is shown in Table S1 in ESI†.
- Significantly, isomerisation of the alkynol **4a** to the corresponding enal **5a** with the rhenium(V)-catalyst [ReOCl<sub>3</sub>(OPPh<sub>3</sub>)(SMe<sub>2</sub>)] in a 5 mol% loading at 80 °C requires (20 h) (see ref. 8f). This isomerisation with our previously reported catalytic systems Ru(II)/CF<sub>3</sub>CO<sub>2</sub>H requires 1.5 h (see ref. 5a).
- This total E-stereoselectivity was also previously observed for the rhenium(V)-catalyst [ReOCl<sub>3</sub>(OPPh<sub>3</sub>)(SMe<sub>2</sub>)] (ref. 8f).
- The limitation of this methodology concerns to the use of primarily propargylic alcohols as the propargylic alcohol (HC≡CCH<sub>2</sub>OH) give rise to a polymer material.
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- The presence of catalytic amounts (5 mol%) of complex **3b** was found to be essential for the reaction outcome. Note that in the absence of the catalyst the reaction did not generate any product (see Table S2 in ESI†).
- In our case, the use of MW as heating source slowed down the reaction; as an example, using 5 mol% of complex **3b** under a N<sub>2</sub> atmosphere at 80 °C with 300 MW, only 35% conversion of 1,1-diphenyl-2-propyn-1-ol into 3,3-diphenylpropenal in [BMIM][PF<sub>6</sub>] was achieved after 1 hour.
- The oxo-rhenium(V) catalyst [ReOCl<sub>3</sub>(OPPh<sub>3</sub>)(SMe<sub>2</sub>)] remains active only for two cycles requiring 20 h, see ref. 8f.