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Cyclisation of acetylenic carboxylic acids and acetylenic alcohols to oxygen-containing heterocycles using cationic rhodium(I) complexes

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Dedicated to Professor Martin Bennett — an inspirational chemist who has contributed to the fundamental understanding of Organometallic Chemistry and the training of generations of Organometallic Chemists.

Abstract

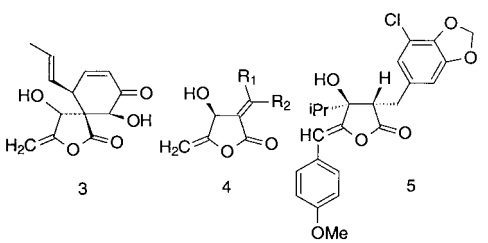
Square planar cationic rhodium(I) dicarbonyl complexes $[\{Rh((mim)_2CH_2)(CO)_2\}^+BPh_4^-]$ (**1**) and $[\{Rh((mBnzim)_2CH_2)(CO)_2\}^+BPh_4^-]$ (**2**) [mim = *N*-methylimidazol-2-yl, mBnzim = *N*-methylbenzimidazol-2-yl] are catalysts for the cyclisation of alkynoic acids to lactones. The unsaturated acids, 4-pentynoic acid, 4-hexynoic acid and 5-hexynoic acid were cyclised to γ-methylene-γ-butyrolactone, *E*-5-ethylidenetetrahydro-2-furanone and 6-methylidenetetrahydo-2-pyrone, respectively. Cyclisation of 4-hexynoic acid proceeds stereoselectively with exclusive formation of the *E*-isomer of 5-ethylidenetetrahydro-2-furanone. Complexes **1** and **2** also catalyse cyclisation of acetylenic alcohols to oxygen-containing heterocycles. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Rhodium; Carbonyl; Cationic; Catalysts; Cyclisation of alkynoic acids

1. Introduction

Transition metal complexes have been used extensively in the synthesis of carbocyclic [1–3] and heterocyclic [4–8] compounds. Organometallic complexes have been particularly successful in the synthesis of five- and six-membered oxygen-containing heterocycles starting from alken-ol [9], alkyn-ol [5,10–15], enyne and dienyne precursors [3,16,17], as well as other substrates [18,19].

Saturated and unsaturated five- and six-membered ring systems containing oxygen are prevalent in natural products and are also commercially important, with applications in pharmaceuticals, flavours and fragrances. Exocyclic enol lactones are important as synthetic intermediates [20], and interest in synthetic methods for the preparation of exocyclic enol lactones has arisen because of the biological activity exhibited by a number of natural products containing this substructure, e.g. paecilospirone (**3**) [21], the linderanolides, isolinderanolides, obtusilactones and isoobtusilactones (**4**) [22] and cyanobacterin (**5**) [23a]. Compounds containing the exocyclic enol lactone fragment are reported to have cytotoxic and antibiotic properties [23].



Synthetic approaches to five-membered exocyclic enol lactones based on the metal-catalysed cyclisation of 4-alkynoic acids have used rhodium, palladium and mercury complexes as catalysts [7,13–15,24,25]. Arcadi

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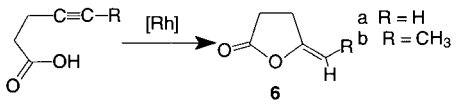
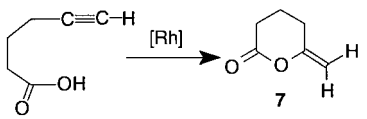


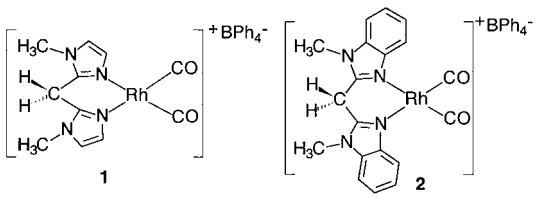
Scheme 1.



Scheme 2.

et al. [15,19] have reported a stereoselective palladium catalysed procedure for the preparation of a range of five-membered exocyclic enol lactones and six-membered exocyclic enol lactones using metal catalysed cyclisation of 5-hexynoic acid. Lewis acids including mercury-based [11–14,24] and silver-based [26] catalysts have also been reported to cyclise alkynoic acids however, a novel catalyst with a cuboidal $PdMo_3S_4$ core has been reported to catalyse the cyclisation of alkynoic acids to enol lactones with significantly higher efficiency [27].

We have recently reported that the cationic Rh(I) complexes $[\{Rh((mim)_2CH_2)(CO)_2\}^+BPh_4^-]$ (**1**) and $[\{Rh((mBnzim)_2CH_2)(CO)_2\}^+BPh_4^-]$ (**2**) [mim = *N*-methylimidazol-2-yl, mBnzim = *N*-methylbenzimidazol-2-yl] are effective catalysts for the intramolecular hydroamination of acetylenic amines [28] to form five- and six-membered ring nitrogen heterocycles.



In this paper we report the cyclisation of acetylenic carboxylic acids to enol-lactones, and acetylenic alcohols to other oxygen-containing heterocyclic compounds using **1** and **2** as catalysts.

2. Results and discussion

2.1. Cyclisation of alkynoic acids to form exocyclic enol lactones

4-Pentynoic acids, are cyclised to γ-methylene-γ-butyrolactones (**6**) (Scheme 1), and 5-hexynoic acid is cyclised to 6-methylidenetetrahydo-2-pyrone (**7**) (Scheme 2).

2.1.1. 4-Pentynoic acids

The cyclisation of 4-pentynoic acid to form γ-methylene-γ-butyrolactone (α′-angelicalactone) (**6a**) was catalysed by rhodium complexes $[\{Rh((mim)_2CH_2)(CO)_2\}^+BPh_4^-]$ (**1**) and $[\{Rh((mBnzim)_2CH_2)(CO)_2\}^+BPh_4^-]$ (**2**) (Scheme 2, R = H). The cyclisation is rapid and clean in the presence of either **1** or **2**, and ca. 260 turnovers (~ 95% conversion) were observed after 15.5 h at 50°C. The product **6a** was the only product formed in the reaction and was identified by comparison of the NMR data with literature NMR data [14].

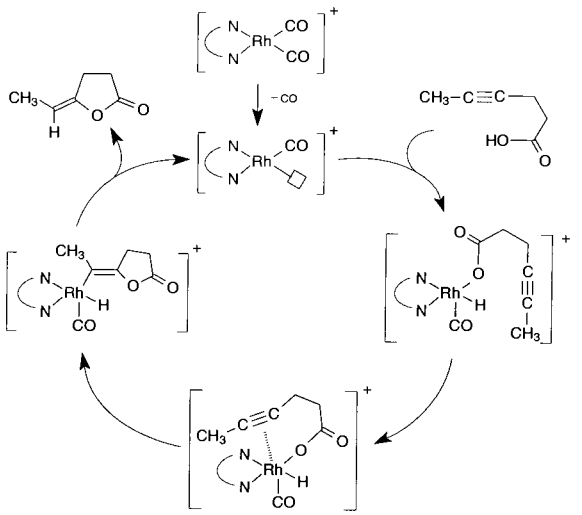
There have been several reports of the cyclisation of 4-pentynoic acid, catalysed by metal complexes including $Pd(PPh_3)_4$ [7], $Rh(PPh_3)_3Cl$ [7], Hg(OAc) [14], $[Rh(PPh_3)_4]Cl$ [29] and $[Rh(cyclophos)Cl]_2$ [7] [cyclophos = 1,2-bis(dicyclohexylphosphino)ethane]. The rates of catalysis for the conversion of 4-pentynoic acid to **6a** using **1** and **2** as catalysts were considerably greater than those previously reported using other metal complexes or metal salts (Table 1). Although none of the literature reports have involved a careful kinetic analysis, it is apparent that the catalytic efficiency of both **1** and **2** appears to be better than or comparable to the best reported catalysts for this cyclisation.

4-Hexynoic acid is a non-terminal carboxylic acid and its cyclisation to the corresponding exocyclic enol lactone was catalysed by the complex $[\{Rh((mim)_2CH_2)(CO)_2\}^+BPh_4^-]$ (**1**). The cyclisation of 4-hexynoic acid formed *E*-5-ethylidenetetrahydro-2-

Table 1
Comparison of rates of cyclisation of 4-pentynoic acid to γ-methylene-γ-butyrolactone, catalysed by metal catalysts

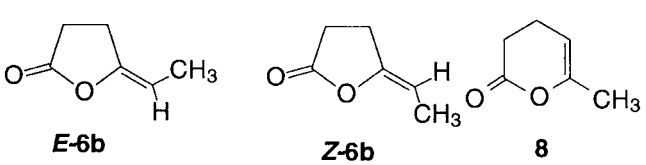
Catalyst	Yield (%)	Catalyst loading (mol%)	Time (h)	Reference
1 [a]	88	0.35	15.5	This work
2 [a]	98	0.4	15.5	This work
$[Rh(cyclophos)Cl]_2$ [b]	93	2.0	24	[7]
$Pd(PPh_3)_4$ [b]	81	4.0	16	[7]
$Rh(PPh_3)_3Cl$ [b]	48	4.0	72	[7]
Hg(OAc) [b]	93	2.0	24	[14]
Ag_2CO_3 [c]	95	10.0	2	[26]

[a] Reactions performed at 50°C.
[b] Reactions performed at room temperature.
[c] Reaction performed at 80°C.



Scheme 3.

furanone (**6b**) exclusively, with 26% conversion (ca. 120 turnovers) after 14.5 h at 50°C (Scheme 2). Cyclisation of 4-hexynoic acid proceeded more slowly than cyclisation of the corresponding terminal acetylene (4-pentynoic acid) and resulted in the exclusive formation of the *E*-isomer. The stereochemistry of the product was established by comparison of ^{1}H-NMR data with literature data [7,24,30]. The stereoselectivity of this reaction is notable-cyclisations of 4-hexynoic acid which have been reported previously for a range of different catalysts are generally not selective and lead to a mixture of products [7], including the *E*- or *Z*-isomers of 5-ethylidenetetrahydro-2-furanone (***E*-6b, *Z*-6b**) and the six-membered ring lactone 6-methyl-3,4-dihydro-2-pyrone (**8**). The chloride-bridged dimer complex [Rh(cyclophos)Cl]$_2$ has been reported to cyclise 4-hexynoic acid to ***Z*-6b** with high selectivity [7].



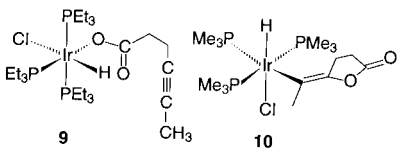
***E*-6b** ***Z*-6b** **8**

2.1.2. 5-Hexynoic acid

In the presence of [{Rh((mim)$_2$CH$_2$)(CO)$_2$}$^+$BPh$_4^-$] (**1**), 5-hexynoic acid was cyclised to 6-methylidenetetrahydo-2-pyrone (**7**) (Scheme 2). The cyclisation reaction was considerably slower than the formation of the corresponding five-membered ring products. The reaction proceeded to 80% conversion (110 turnovers) using 0.7 mol% of the rhodium complex **1** as catalyst after 8 days at 50°C. The identity of the product **7** was confirmed by comparison of the ^{1}H-NMR data with literature data [13]. The rates for the cyclisation of 5-hexynoic acid are similar to the rates reported in the literature [7,11].

2.1.3. Mechanistic considerations

A mechanism by which the cyclisation of the 4-pentynoic acid and 4-hexynoic acid takes place has been proposed previously for other rhodium [7], iridium [24] and palladium [15] complexes. In the case of iridium, which shows little catalytic activity, a number of stable organometallic species have been isolated from reactions and characterised crystallographically (**9** and **10**) [24] and these are reasonable intermediates in the cyclisation reaction.



9 **10**

The mechanism proposed for the cyclisation of 4-hexynoic acid by [Rh(cyclophos)Cl]$_2$ involves the initial oxidative addition of the –O–H bond of the carboxylic acid followed by coordination of the acetylene with loss of carboxylate and subsequent nucleophilic attack of the pendant carboxylate on the activated alkyne. This mechanism accounts for the selectivity observed for the formation of the *Z*-isomer and justifies the similarity of the product distribution to that observed with more traditional Lewis acid catalysts.

The mechanism for the cyclisation of alkynoic acids by **1** must differ from that proposed for other catalyst systems since it must account for the exclusive formation of the *E*-isomer of 5-ethylidenetetrahydro-2-furanone (***E*-6b**) from 4-hexynoic acid. The formation of the *E*-isomer suggests that the carboxylate is not lost from the metal centre prior to attack on the alkyne and that the addition is directed from the metal centre (Scheme 3).

In this mechanism, migratory insertion delivers the oxygen to the coordinated alkyne from metal centre, ensuring the *E*-stereochemistry in the product.

2.2. Cyclisation of acetylenic alcohols

The cyclisation of the acetylenic alcohol 4-pentyn-1-ol leads to the formation of a five-membered ring cyclic acetal in which a molecule of alcohol (either from the solvent or a second molecule of the starting alcohol) is incorporated into the product. The cyclisation works well for terminal 4-pentynols — no reaction was observed with 4- or 6-carbon terminal alkynols or for compounds containing for non-terminal alkynes.

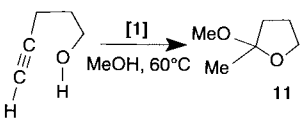
2.2.1. Cyclisation of 4-pentyn-1-ol in alcoholic solvents

The cyclisation of 4-pentyn-1-ol in methanol solvent catalysed by complexes **1** and **2** results in the formation of 2-methyl-2-methoxy-3,4,5-trihydrofuran (**11**) and proceeds to completion even at room temperature. The reaction occurs at a rate of ca. 25 turnovers per h using

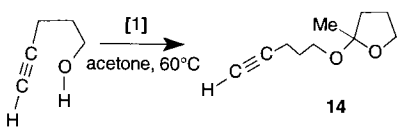
ca. 1 mol% of complex **1** or **2** as catalyst at 60°C. The product results from cyclisation of the 4-pentyn-1-ol with incorporation of methanol (solvent) at position 2 of the tetrahydrofuran ring (Scheme 4). The exocyclic methyl group is derived from the terminal carbon of the alkyne.

The heterocycle **11** was fully characterised by ^{1}H- and ^{13}C-NMR spectroscopy. A 2D NOESY spectrum was used for complete assignment of the proton spectrum.

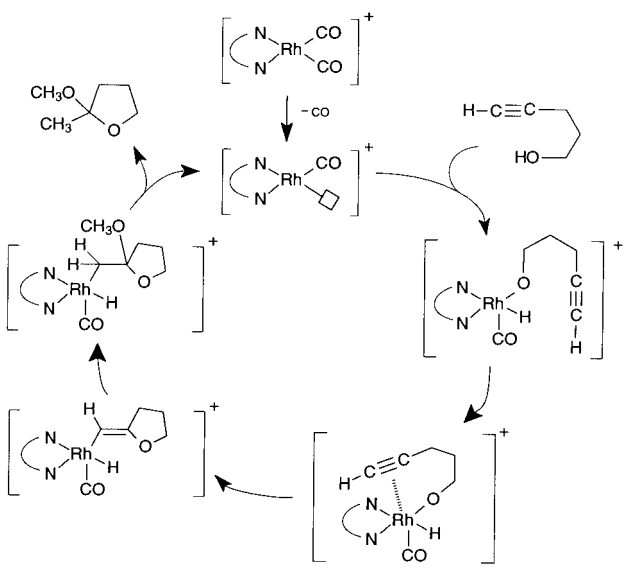
Cyclisation of 4-pentyn-1-ol in ethanol rather than methanol solvent, but otherwise under identical conditions to those described for the formation of **11**, afforded 2-methyl-2-ethoxy-3,4,5-trihydrofuran (**12**). The reaction occurred at a similar rate to the reaction in methanol solvent.



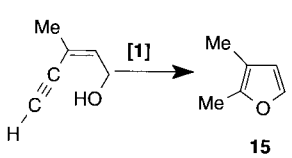
Scheme 4.



Scheme 5.

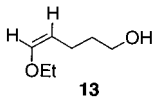


Scheme 6.



Scheme 7.

In cyclisation reactions of 4-pentyn-1-ol in alcohol solvent, an organic bi-product was observed (ca. 10–15%) which, in the case of reactions with ethanol solvent, was identified as the enol ether **13.**



The product **13** results from net addition of ethanol solvent across the triple bond. Only the product with *cis* stereochemistry was observed.

2.2.2. Cyclisation of 4-pentyn-1-ol in the absence of alcohol solvent

In non-alcohol solvents, cyclisation of 4-pentyn-1-ol resulted in formation of 2-methyl-2-(4-pentynyloxy)-3,4,5-trihydrofuran (**14**) (Scheme 5). This compound arises from cyclisation followed by reaction of the alcohol functionality of free 4-pentyn-1-ol. The complete assignment of the ^{1}H-NMR and ^{13}C-NMR spectra was achieved using 2D-NMR techniques.

The cyclisation reaction of 4-pentyn-1-ol to form **14** was significantly slower than in alcohol solvent with only 20–30% product formation after 4 h at 60°C.

2.2.3. Mechanistic considerations

No intermediate transition metal complexes were observed in the cyclisation of 4-pentyn-1-ol and organometallic bi-products have not been identified. Given the fact that the cyclisation of acetylenic alcohols was observed only for terminal acetylenes, the cyclisation could be rationalised by initial addition of either the terminal acetylene or the O–H group. Scheme 6 depicts a mechanism that is consistent with the experimental observations and analogous to that proposed for the cyclisation of acetylenic carboxylic acids. The initial step involves oxidative addition of the O–H group to the rhodium centre with loss of CO and coordination of the pendant acetylene. Migratory insertion produces the coordinated cyclic vinyl ether, which could add an alcohol to the vinyl group and reductive elimination of the organic product regenerates the reactive metal complex. Alternatively, reductive elimination from the metal vinyl ether would produce a vinyl ether which would be trapped by the alcohol solvent.

The observed formation of the vinyl ether bi-product (**13**) can be rationalised as the result of intermolecular addition of an alcohol to the coordinated activated acetylene.

2.2.4. Cyclisation of cis-3-methyl-2-pentene-4-yn-1-ol

The cyclisation of *cis*-3-methyl-2-pentene-4-yn-1-ol to form 2,3-dimethylfuran (**15**) occurred in the presence of a catalytic quantity of [{Rh((mim)$_2$CH$_2$)(CO)$_2$}$^+$-BPh$_4^-$}] (**1**) or [{Rh((mBnzim)$_2$CH$_2$)(CO)$_2$}$^+$BPh$_4^-$}] (**2**)

(Scheme 7). The rate was ca. 11 turnovers per hour of the starting material to product at a loading of 0.3 mol% of **1** at 50°C, and ca. 4.3 turnovers per hour at a loading of 0.7 mol% of **2** at 50°C. Complexes **1** and **2** were significantly less efficient as catalysts in this cyclisation than the most efficient ruthenium complex reported [$Ru(PPh_3)(p\text{-cymene})Cl_2$] [6], (1000 turnovers in 2 h with 100% conversion), however, the rates were comparable to those reported for a number of other catalysts [31].

The cyclisation is specific to the terminal acetylene; the non-terminal analogue where the acetylene was methylated, *cis*-3-methyl-2-hexene-4-yn-1-ol, does not undergo cyclisation in the presence of either **1** or **2**.

3. Conclusions

The complexes [$\{Rh((mim)_2CH_2)(CO)_2\}^+BPh_4^-$] (**1**) or [$\{Rh((mBnzim)_2CH_2)(CO)_2\}^+BPh_4^-$] (**2**) (and also related derivatives) show good promise as catalysts for the intramolecular addition of O–H bonds to carbon–carbon triple bonds. They are efficient catalysts for the formation of oxygen containing heterocycles from acetylenic alcohols and carboxylic acids. Acetylenic acids were cleanly cyclised to lactones and in the catalytic cyclisation of 4-hexynoic acid, only *E*-5-ethylidenetetrahydro-2-furanone was formed and the observed stereoselectivity is a significant improvement over that reported with other catalysts for this cyclisation.

Acetylenic alcohols were efficiently cyclised in the presence of **1** and **2** as catalysts in alcohol solvents. The product acetals incorporate one molecule of the solvent and their formation can be rationalised by the addition of an alcohol to an intermediate vinyl metal species. Cyclisation of *cis*-3-methyl-2-pentene-4-yn-1-ol to 2,3-dimethylfuran was catalysed by both **1** and **2**.

4. Experimental

4.1. General procedures

All manipulations of metal complexes and air sensitive reagents were carried out using standard Schlenk or vacuum techniques [32], or in a Vacuum Atmospheres argon-filled dry-box.

Tetrahydrofuran, benzene, hexane and toluene were stored over sodium wire and were distilled under nitrogen immediately prior to use from sodium benzophenone ketyl. Absolute ethanol and methanol were distilled from magnesium turnings. Acetone was dried over and distilled from anhydrous calcium sulfate.

The terminal acetylenes were commercially available, and the non-terminal acetylenes were synthesised by alkylation of the terminal alkyne analogues [33]. 4-Pentyn-1-ol, *cis*-3-methyl-2-pentene-4-yn-1-ol and 4-pentynoic acid were purchased from Aldrich and used without further purification. 4-Hexynoic acid and 5-hexynoic acid were prepared by the method of Holland et al. [34].

All bulk compressed gases were obtained from British Oxygen Company (BOC Gases). Argon ($>99.99\%$), nitrogen ($>99.5\%$) and carbon monoxide ($>99.5\%$) were used as supplied without further purification.

4.2. Cyclisation of 4-pentynoic acid to γ-methylene-γ-butyrolactone (α′-angelicalactone, **6a**)

4.2.1. Catalysed by [$\{Rh((mim)_2CH_2)(CO)_2\}^+BPh_4^-$] (**1**)

[$\{Rh((mim)_2CH_2)(CO)_2\}^+BPh_4^-$] (**1**) (2.8 mg, 4.11 μmol) was added to 4-pentynoic acid (120 mg, 1.2 mmol) in acetone-d_6 (0.3 ml) and benzene (0.4 g, internal standard) in a NMR tube. The mixture was heated at 50°C for 15.5 h, after this time the peaks corresponding to starting material and product were integrated relative to the internal standard (benzene). The product, γ-methylene-γ-butyrolactone (**6a**), was obtained as the only product. Compound **6a** was purified by passing down a short column of flash silica with ether as eluent, followed by removal of the ether solvent under vacuum. γ-Methylene-γ-butyrolactone was obtained as a colourless oil (106 mg, 88%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.68 (m, 1H, C=CH_2), 4.27 (m, 1H, C=CH_2), 2.88–2.81 (m, 1H, *H*4), 2.66–2.60 (m, 2H, *H*3). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): δ 175.6 (*C*=O), 156.4 (*C*=CH_2), 89.2 (C=*C*H_2), 28.6 (*C*H_2), 25.7 (*C*H_2). Spectroscopic data was consistent with that reported in the literature [14].

4.2.2. Catalysed by [$\{Rh((mBnzim)_2CH_2)(CO)_2\}^+BPh_4^-$] (**2**)

[$\{Rh((mBnzim)_2CH_2)(CO)_2\}^+BPh_4^-$] (**2**) (6.0 mg, 7.6 μmol) was added to 4-pentynoic acid (200 mg, 2.0 mmol) in acetone-d_6 (0.3 ml) and benzene (0.4 g, internal standard) in a NMR tube. The mixture was heated at 50°C for 15.5 h, after this time the product γ-methylene-γ-butyrolactone (**6a**) was formed in 98% conversion from starting material [36]. The product was isolated by chromatography as described above.

4.3. Cyclisation of 4-hexynoic acid to E-5-ethylidenetetrahydro-2-furanone (**6b**)

[$\{Rh((mim)_2CH_2)(CO)_2\}^+BPh_4^-$] (**1**) (1.3 mg, 1.9 μmol) was added to a solution of 4-hexynoic acid (96 mg, 0.86 mmol) in acetone-d_6 (0.3 ml) in a NMR tube. The mixture was heated at 50°C for 14.5 h. The product, *E*-5-ethylidenetetrahydro-2-furanone (**6b**), was

formed in a yield of 26% [36] from starting material and isolated by chromatography as described above. Spectroscopic data were consistent with literature data [7,24,30]. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.54 (m, 1H, $^3J_{CH-CH_3} = 7.0$ Hz, $^4J_{H-C=C-CH} = 2.0$ Hz, C=C*H*), 2.78–2.53 (m, 4H, 2 × CH_2), 1.57 (dt, 3H, $^3J_{CH_3-CH} = 7.0$ Hz, $^5J_{H-H} = 2.0$ Hz, CH_3). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$): δ 175.9 (*C*=O), 149.0 (*C*=C(CH_3)H), 99.7 (C=*C*(CH_3)H), 28.6 (*C*H_2), 25.5 (*C*H_2), 10.9 (*C*H_3).

4.4. Cyclisation of 5-hexynoic acid to 6-methylideneterahydo-2-pyrone (7)

[{Rh((mim)$_2$CH$_2$)(CO)$_2$}$^+$BPh$_4^-$] (**1**) (5.0 mg, 7.3 μmol) was added to a solution of 5-hexynoic acid (110 mg, 1.0 mmol) in acetone-d_6 (0.3 ml) in a NMR tube. The mixture was heated at 50°C for 8 days. The product, 6-methylidenetetrahydo-2-pyrone (**7**), was formed in 80% conversion from starting material [35]. Spectroscopic data were consistent with literature data [13].

^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.52 (m, 1H, =CH_2), 4.25 (m, 1H, =CH_2), 2.59 (t, 2H, $J = 6.8$ Hz, CH_2), 2.46 (m, 2H, CH_2), 1.83 (m, 2H, *CH*$_2$). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$): δ 168.9 (C=O), 156.0 (*C*=CH_2), 94.3 (C=*C*H_2), 30.9 (*C*H_2), 27.3 (*C*H_2), 19.2 (*C*H_2).

4.5. Cyclisation of 4-pentyn-1-ol in methanol to 2-methyl-2-methoxy-3,4,5-trihydrofuran (11)

4.5.1. Catalysed by [{Rh((mim)$_2$CH$_2$)(CO)$_2$}$^+$BPh$_4^-$] (1)

4-Pentyn-1-ol (180 mg, 2.1 mmol) was added to a solution of [{Rh((mim)$_2$CH$_2$)(CO)$_2$}$^+$BPh$_4^-$] (**1**) (12 mg, 0.018 mmol) in acetone-d_6 (0.2 ml) and MeOH (0.25 ml) in a NMR tube. The mixture was heated at 60°C in an oil bath for 4 h. The product, 2-methyl-2-methoxy-3,4,5-trihydrofuran (**11**) was formed in 91% conversion from starting material [35]. ^{1}H-NMR (600 MHz, acetone-d_6): δ 3.97 (m, 2H, $H5_B$ and $H5_A$), 3.31 (s, 3H, OCH_3), 2.20–2.07 (m, 2H, $H3_A$ and $H4_B$), 2.06–1.95 (m, 1H, $H4_A$), 1.93–1.83 (m, 1H, $H3_B$), 1.53 (s, 3H, CH_3). ^{13}C{^{1}H}-NMR (100 MHz, acetone-d_6): δ 105.5 (*C2*), 65.2 (*C5*), 35.6 (*C3*), 45.5 (O*C*H_3), 22.4 (*C4*), 18.7 (*C*H_3).

4.5.2. Catalysed by [{Rh((mBnzim)$_2$CH$_2$)(CO)$_2$}$^+$BPh$_4^-$] (2)

4-Pentyn-1-ol (180 mg, 2.1 mmol) was added to a solution of [{Rh((mBnzim)$_2$CH$_2$)(CO)$_2$}$^+$BPh$_4^-$] (**2**) (13 mg, 0.017 mmol) in acetone-d_6 (0.2 ml) and MeOH (0.25 ml) in a NMR tube. The mixture was heated at 60°C in an oil bath for 4 h. The product, 2-methyl-2-methoxy-3,4,5-trihydrofuran (**11**), was formed in 80% [35] conversion from starting material.

4.6. Cyclisation of 4-pentyn-1-ol in the presence of ethanol to 2-methyl-2-ethoxy-3,4,5-trihydrofuran (12)

4.6.1. Catalysed by [{Rh((mim)$_2$CH$_2$)(CO)$_2$}$^+$BPh$_4^-$] (1)

4-Pentyn-1-ol (180 mg, 2.1 mmol) was added to [{Rh((mim)$_2$CH$_2$)(CO)$_2$}$^+$BPh$_4^-$] (**1**) (12 mg, 0.018 mmol) in acetone-d_6 (0.2 ml) and EtOH (0.25 ml) in a NMR tube. The mixture was heated at 60°C in an oil bath for 4 h. 2-Methyl-2-ethoxy-3,4,5-trihydrofuran (**12**) was formed in 80% conversion from starting material [35]. ^{1}H-NMR (600 MHz, acetone-d_6): δ 3.98 (m, 2H, $H5_B$ and $H5_A$), 3.66 (dq, 1H, $^2J_{H-C-H} = 9.1$ Hz, $^3J_{H-H} = 7.0$ Hz, OCH_AH_B), 3.60 (dq, 1H, $^2J_{H-C-H} = 9.1$ Hz, $^3J_{H-C-H} = 7.0$ Hz, OCH_AH_B), 2.22–2.10 (m, 2H, $H3_A$ and $H4_B$), 2.07–1.96 (m, 1H, $H4_A$), 1.91–1.81 (m, 1H, $H3_B$), 1.55 (s, 3H, CH_3), 1.26 (dd, $^3J_{CH3-CHA} = 7.1$ Hz, $^3J_{CH3-CHB} = 7.1$ Hz, OCH$_2$CH_3). ^{13}C{^{1}H}-NMR (100 MHz, acetone-d_6): δ 106.2 (*C2*), 66.0 (*C5*), 54.8 (OCH_2CH$_3$), 37.0 (*C3*), 23.4 (*C*4), 20.6 (*C*H_3), 14.4 (OCH$_2$*C*H_3).

A second product *cis*-EtOCH=CH(CH$_2$)$_3$OH (**13**) was obtained as a minor component (10% conversion from starting material). ^{1}H-NMR (600 MHz, acetone-d_6): δ 6.47 (dt, 1H, $^3J_{H-C=C-H} = 6.3$ Hz, $^4J_{H-H} = 1.9$ Hz, EtOC*H*=CH), 4.78 (m, 1H, $^3J_{H-C=C-H} = 6.3$ Hz, $^3J_{H-H} = 3.6$ Hz, EtOCH=C*H*), 4.09 (m, 2H, HOCH_2), 3.60 (q, 2H, $^3J_{CH2-CH3} = 7.0$ Hz, OCH_2CH$_3$), 2.14 (m, 2H, CH_2), 1.99 (m, 2H, CH_2), 1.28 (t, 3H, $^3J_{CH3-CH2} = 7.0$ Hz, OCH$_2$CH_3). ^{13}C{^{1}H}-NMR (100 MHz, acetone-d_6): δ 143.0 (EtO*C*H=CH), 99.1 (EtOCH=*C*H), 64.31 (*C*H$_2$OH), 54.4 (O*C*H$_2$CH$_3$), 21.7 (CH_2), 18.4 (CH_2), 14.0 (OCH$_2$*C*H$_3$).

4.6.2. Catalysed by [{Rh((mBnzim)$_2$CH$_2$)(CO)$_2$}$^+$BPh$_4^-$] (2)

4-Pentyn-1-ol (180 mg, 2.1 mmol) was added to a solution of [{Rh((mBnzim)$_2$CH$_2$)(CO)$_2$}$^+$BPh$_4^-$] (**2**) (10.5 mg, 0.013 mmol) in acetone-d_6 (0.2 ml) and EtOH (0.25 ml) in a NMR tube. The mixture was heated at 60°C in an oil bath for 4 h. 2-Methyl-2-ethoxy-3,4,5-trihydrofuran (**12**) was formed in 68% conversion from starting material [35].

A second product (**13**) was obtained as a minor component (14% conversion from starting material) in the reaction mixture.

4.7. Cyclisation of 4-Pentyn-1-ol to 2-methyl-2-(4-pentynyloxy)-3,4,5-trihydrofuran (14)

4.7.1. Catalysed by [{Rh((mim)$_2$CH$_2$)(CO)$_2$}$^+$BPh$_4^-$] (1)

4-Pentyn-1-ol (150 mg, 1.8 mmol) was added to a solution of [{Rh((mim)$_2$CH$_2$)(CO)$_2$}$^+$BPh$_4^-$] (**1**) (9.0 mg, 0.013 mmol) in acetone-d_6 (0.3 ml) in a NMR tube. The mixture was heated at 60°C in an oil bath for 4 h.

The product, 2-methyl-2-(4-pentynyloxy)-3,4,5-trihydrofuran (**14**), was formed in 19% conversion from starting material [35]. ^{1}H-NMR (600 MHz, acetone-d_6): δ 3.87–3.81 (m, 2H, $H5_A$, $H5_B$), 3.56–3.51 (m, 1H, OCH_AH_B), 3.51–3.45 (m, 1H, OCH_AH_B), 2.30–2.28 (m, 1H, C≡C*H*), 2.27 (m, 2H, CH_2C≡CH), 2.07–2.01 (m, 1H, $H4_B$), 2.01–1.96 (m, 1H, $H3_B$), 1.91–1.85 (m, 1H, $H4_A$), 1.75–1.68 (m, 1H, $H3_A$), 1.73–1.68 (m, 2H, CH_2CH_2C≡CH), 1.40 (s, 3H, CH_3). ^{13}C{^{1}H}-NMR (100 MHz, acetone-d_6): δ 106.9 (*C2*), 83.7 (*C*≡CH), 68.7 (C≡*C*H), 66.9(*C5*), 58.6 (OCH_2), 37.8 (*C3*), 29.5 (OCH_2CH_2), 24.3 (*C4*), 21.3 (CH_3), 14.8 (CH_2C≡CH).

4.7.2. Catalysed by $[\{Rh((mBnzim)_2CH_2)(CO)_2\}^+BPh_4^-]$ (2)

4-Pentyn-1-ol (180 mg, 2.1 mmol) was added to a solution of $[\{Rh((mBnzim)_2CH_2)(CO)_2\}^+BPh_4^-]$ (**2**) (13 mg, 0.017 mmol) in acetone-d_6 (0.3 ml) in a NMR tube. The mixture was heated at 60°C in an oil bath for 4 h. The product, 2-methyl-2-(4-pentynyloxy)-3,4,5-trihydrofuran (**14**), was formed in 30% conversion from starting material [35].

4.8. Cyclisation of cis-3-methyl-2-pentene-4-yn-1-ol to 2,3-dimethylfuran (15)

4.8.1. Catalysed by $[\{Rh((mim)_2CH_2)(CO)_2\}^+BPh_4^-]$ (1)

cis-3-Methyl-2-pentene-4-yn-1-ol (155 mg, 1.61 mmol) was added to a solution of $[\{Rh((mim)_2CH_2)(CO)_2\}^+BPh_4^-]$ (**1**) (3.7 mg, 5.4 μmol) in acetone-d_6 (0.3 ml) and benzene (0.4 g, internal standard) in a NMR tube. The mixture was heated at 50°C for 26.5 h. The product 2,3-dimethylfuran (**15**) was formed in 93% conversion from starting material [1,36]. Spectroscopic data were consistent with literature data [31]. ^{1}H-NMR (400 MHz, acetone-d_6): δ 7.30 (d, 1H, $^3J_{H5-H4} = 1.9$ Hz, *H5*), 6.21 (d, 1H, $^3J_{H5-H4} = 1.9$ Hz, *H4*), 2.20 (s, 3H, C(2)CH_3), 1.96 (s, 3H, C(3)CH_3).

^{13}C{^{1}H}-NMR (100 MHz, acetone-d_6): δ 146.9 (*C2*), 139.6 (*C5*), 113.5 (*C3*), 112.6 (*C4*), 10.2 (C2–CH_3), 8.8 (C3–CH_3).

4.8.2. Catalysed by $[\{Rh((mBnzim)_2CH_2)(CO)_2\}^+BPh_4^-]$ (2)

cis-3-Methyl-2-pentene-4-yn-1-ol (90 mg, 0.94 mmol) was added to a solution of $[\{Rh((mBnzim)_2CH_2)(CO)_2\}^+BPh_4^-]$ (**2**) (4.8 mg, 6.1 μmol) in acetone-d_6 (0.3 ml) and benzene (0.4 g, internal standard) in a NMR tube. The mixture was heated at 50°C for 21.5 h. The product 2,3-dimethylfuran (**15**) was formed in 60% conversion from starting material [36].

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