EurJIC European Journal of Inorganic Chemistry

ChemPubSoc Europe

FULL PAPER

DOI:10.1002/ejic.201300651

Glycerol – A Non-Innocent Solvent for Rh-Catalysed Pauson–Khand Carbocyclisations

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Keywords: C–C coupling / Rhodium / Reaction mechanisms / NMR spectroscopy / Glycerol

Rh-catalysed carbocyclisations of the 1,6-enynes **1**–**8** efficiently gave bicyclo[3.3.0]octenones in neat glycerol. Unexpectedly, ligand-free [Rh(μ-OMe)(cod)]$_2$ was highly selective. Moreover, TPPTS [tris(3-sulfonatophenyl)phosphane trisodium salt] improved the catalyst performance at low Rh/L ratios, but surprisingly, ligand excess blocked the reaction. Detailed NMR studies evidenced the role of glycerol in the catalytic process.

Introduction

The synthesis of highly functionalised organic molecules often results in large amounts of waste products because of the multitude of reagents and the number of purification steps involved, which leads to a strong negative environmental impact and expensive processes. Thus, the development of multi-step syntheses, in which several bonds are formed in "one-pot" reactions, is a good tool to reduce this effect. This solution becomes particularly attractive when one is working under catalytic conditions, in which case it amplifies the atom economy[1] and decreases the required energy, which is in accordance with the green chemistry principles.[2] In the last ten years, alternatives to commonly used organic, volatile solvents have been studied: ionic liquids, water, supercritical fluids, and perfluorinated solvents.[3] However, the general use of such alternatives still has some limitations, such as high cost, a lack of data concerning toxicity and biodegradability, and the separation of products. The Rh-catalysed [2+2+1] Pauson–Khand carbocyclisation reaction (PKR)[4] appeared to us as an excellent example to illustrate the complementarity of these two concepts. The PKR comprises the simultaneous formation of three C–C bonds and the insertion of a carbonyl functionality from carbon monoxide. We chose to develop the PKR in neat glycerol,[5] an innovative solvent in catalysis, which is synthesized from biomass and is currently produced in high amounts as waste in the biodiesel production. Its low cost, non-toxicity, high boiling point, negligible vapour pressure, high solubility for organic and inorganic compounds, and low miscibility with other organic solvents, constitute attractive properties for applications in catalysis. However, the potential reactivity of its hydroxy groups can lead to by-products, mainly, when one is working under strong basic conditions. However, these groups can also participate in acid–base exchanges, inducing positive effects in the elementary catalytic steps.

To the best of our knowledge, the use of glycerol in the PKR represents a pioneering work in the literature. Herein, we report the influence of this medium using the complexes [Rh(μ-X)(cod)]$_2$ (X = OMe$^-$, Cl$^-$) as catalytic precursors. The effect of mono- and diphosphane ligands was also evaluated. A NMR study was carried out to understand the different species that formed depending on the catalytic system.

Results and Discussion

We chose the 1,6-enynes **1**–**3** as model substrates for our preliminary tests concerning the Rh-catalysed PKR in glycerol (Scheme 1).

The use of [Rh(μ-OMe)(cod)]$_2$ as a catalytic precursor afforded active catalytic systems in glycerol, and using the substrates **1**–**3** in the absence of an additional ligand and a silver salt led to 90% (**1a** and **3a**) and 60% (for **2a**) isolated yields (Table 1, entries 1–3). At a shorter reaction time, the bicyclo[3.3.0]octenone **1a** was obtained in high yield (82%, Table 1, entry 4). Surprisingly, under similar conditions, the [Rh(μ-Cl)(cod)]$_2$ precursor was practically inactive for these substrates (conversions <5%). The beneficial influence of glycerol was evidenced by comparison with different or-

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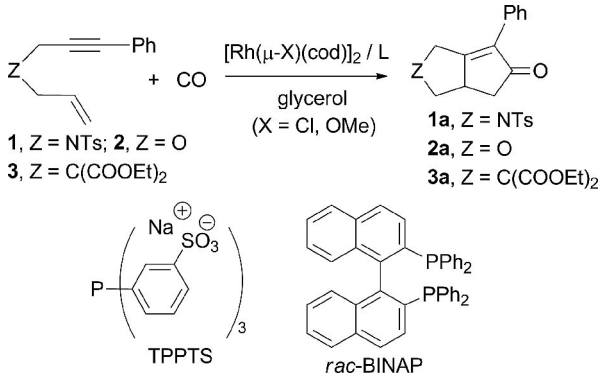
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201300651.



Scheme 1. Rh-catalysed PKR of enynes **1**–**3** (L = TPPTS, *rac*-BINAP).

ganic solvents. Whereas in toluene, a non-coordinating solvent, $[Rh(\mu\text{-OMe})(cod)]_2$ exhibited a low activity (less than 10% conversion for substrates **1** and **2**; Table 1, entries 5 and 6), full conversion of **1** was achieved when the coordinating solvent thf was used. However, in this case, the reaction suffers from a low chemoselectivity (40% yield, Table 1, entry 7). A decrease in the CO pressure for the PKR of **1** in glycerol induced a higher catalytic activity (Table 1, entry 8 vs. 4), which is in agreement with similar observations related to the PKR in conventional organic solvents.[6] In total absence of CO, the system is inactive, evidencing that under these reaction conditions glycerol cannot act as a CO source, which is in contrast to results described in the works of Chung et al.[7] and Morimoto et al.,[8] in which alcohols or aldoses were used as CO sources, respectively.

Aldehydes have also been reported as alternative CO sources for Rh-catalysed PKR.[9] The addition of cinnamaldehyde to our catalytic mixture did not lead to its Rh-catalysed decarbonylation, which is in contrast to previous reports.[10]

To study the influence of phosphanes on the PKR reaction in glycerol, we chose TPPTS (Scheme 1) because of its higher solubility in this medium compared to PPh_3.

Whereas the catalytic system using $[Rh(\mu\text{-OMe})(cod)]_2$/TPPTS in a 1:1 Rh/ligand ratio was very active and selective (up to 90% isolated yield for **1a**, entry 9 in Table 1), the 1:2 Rh/ligand ratio led to an inactive system (Table 1, entry 10). Consistent with these results, when the bidentate ligand *rac*-BINAP (Scheme 1) was used, the corresponding Rh–BINAP system was also inactive (Table 1, entry 11). In an attempt to increase the catalytic activity, $[Rh(\mu\text{-Cl})(cod)]_2$ was treated with silver triflate, but no reaction was detected even after 24 h (Table 1, entry 12). This behaviour strongly contrasts with the data reported for studies with thf as the solvent.[11]

Other related substrates were tested under the best conditions found for substrate **1**, and this proved the high efficiency of the catalytic system (Table 2). The presence of electron-donor groups on the aryl fragment triggers an activity increase (Table 2, entries 1 and 2 vs. 3 and 4), which is in agreement with the trend observed for organic solvents.[10c] Surprisingly, despite a potential Thorpe–Ingold effect, the enyne **8** afforded the corresponding bicyclo[3.3.0]octenone in a slightly lower yield (Table 2, entry 2 vs. 5).

These results evidence a non-innocent role of glycerol in the PKR. We were especially interested in understanding the catalytic influence of the anion bridge of the organometallic precursor and of the ligand. Some NMR experiments were thus carried out to better understand this behaviour.

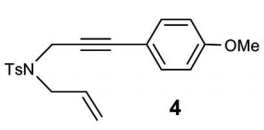
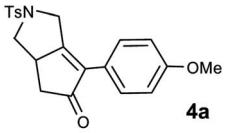
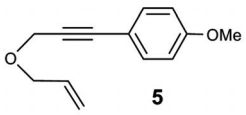
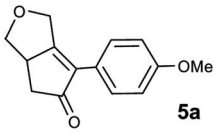
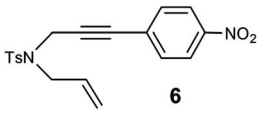
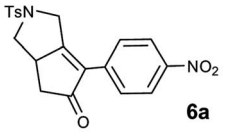
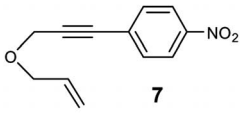
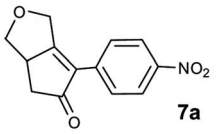
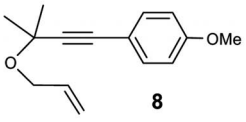
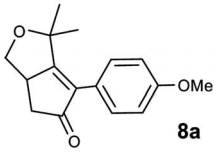
The catalytic activity associated to $[Rh(\mu\text{-OMe})(cod)]_2$ is in contrast to the lack of activity observed with $[Rh(\mu\text{-Cl})(cod)]_2$. This can be associated to the Brønsted-basic character of the methoxide group in a protic medium such as glycerol.[12] To evidence the plausible proton exchange, ^1H and ^{13}C NMR spectra for both organometallic precursors were analysed in CD_2Cl_2\{$[Rh(\mu\text{-X})(cod)]_2$/glycerol = 1:2, X = Cl^-, OMe^-\} (Figs. S1–S4). The ^{13}C NMR spectrum of $[Rh(\mu\text{-OMe})(cod)]_2$ (Figure 1, b) shows the presence of two rhodium species, which can be clearly identified by the signals corresponding to the coordinated cyclooctadiene [two doublets in the methylene region: 78.7 ppm, $J_{Rh-(CH=CH)}$ = 14 Hz; 74.1 ppm, $J_{Rh-(CH=CH)}$ = 14.8 Hz; two singlets in the aliphatic region: 30.9 and 30.6 ppm], be-

Table 1. Rh^I-catalysed Pauson–Khand reaction using **1**, **2** and **3** as 1,6-enynes.[a]

Entry	Enyne	Ligand (Rh/P)	Solvent	p_{CO} [bar]	Reaction time [h]	Temperature [°C]	Conversion[b] (isolated yield) [%]
1	1	–	glycerol	1	16	80	100 (90)
2	2	–	glycerol	1	16	80	100 (60)
3	3	–	glycerol	1	16	80	100 (90)
4	1	–	glycerol	1	4	80	82 (82)
5	1	–	toluene	1	16	reflux	10
6	2	–	toluene	1	16	reflux	5
7	1	–	thf	1	16	reflux	100 (40)
8	1	–	glycerol	0.5	4	80	90 (90)
9	1	TPPTS (1:1)	glycerol	1	4	80	90 (90)
10	1	TPPTS (1:2)	glycerol	1	24	80	0
11	1	*rac*-BINAP (1:1)	glycerol	1	24	80	0
12	1	*rac*-BINAP (1:1)[c]	glycerol	1	24	80	0

[a] Reaction conditions: $[Rh(\mu\text{-OMe})(cod)]_2$ as catalytic precursor; Rh/enyne = 1:20; 5 mL of solvent. [b] Determined by ^1H NMR spectroscopy. [c] $[Rh(\mu\text{-Cl})(cod)]_2$/BINAP/AgOTf = 0.5:1:1.

Table 2. Rh^{I}-catalysed Pauson–Khand reactions using **4**–**8** as 1,6-enynes.[a]

Entry	Substrates and products		Conversion[b] (isolated yield) [%]
1	 **4**	 **4a**	100 (95)
2	 **5**	 **5a**	100 (90)
3	 **6**	 **6a**	80 (70)
4	 **7**	 **7a**	50 (40)
5	 **8**	 **8a**	95 (80)

[a] Reaction conditions: $[Rh(\mu\text{-OMe})(cod)]_2$ as catalytic precursor; Rh/enyne = 1:20; 5 mL of glycerol; 80 °C; 0.5 bar CO; 4 h. [b] Determined by ^{1}H NMR spectroscopy.

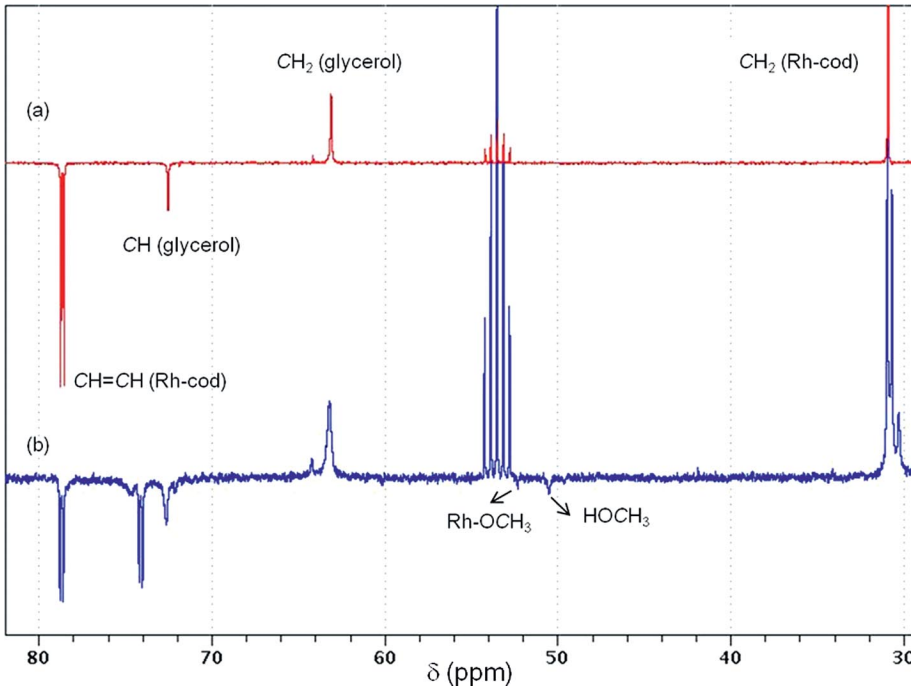
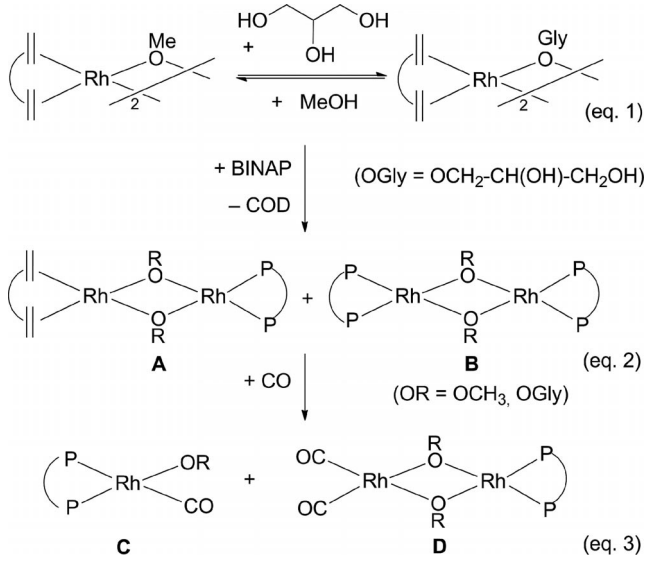


Figure 1. Comparison between ^{13}C NMR spectra (76.5 MHz, CD_2Cl_2, 298 K) of $[Rh(\mu\text{-Cl})(cod)]_2$ (a) and $[Rh(\mu\text{-OMe})(cod)]_2$ (b) in glycerol. Rh/glycerol = 1:1.

sides the appearance of a CH_3OH resonance. This is in contrast to the unique species observed for $[Rh(\mu\text{-}Cl)(cod)]_2$ [δ = 78.6 ppm (d), $J_{Rh-(CH=CH)}$ = 14.9 Hz; 30.9 ppm (s), Figure 1, a].[13] These facts agree with the coexistence of two Rh dimers, in one of which deprotonated glycerol acts as a bridging ligand [Equation (1), Scheme 2].



Scheme 2. Rh^I species generated from $[Rh(\mu\text{-}OMe)(cod)]_2$ in glycerol in the presence of *rac*-BINAP.

Further addition of *rac*-BINAP (Scheme 1) to the $[Rh(\mu\text{-}OMe)(cod)]_2$ glycerol solution leads to the formation of two main rhodium species, as evidenced by the two close doublets observed by ^{31}P NMR spectroscopy (δ = 49.3 ppm, J_{Rh-P} = 207 Hz; 48.9 ppm, J_{Rh-P} = 199 Hz) (Figure 2, top).

In agreement with the literature,[14,15] their Rh–P coupling constants and chemical shifts point to the formation of neutral species, where the diphosphane does not act as a bridging ligand. The ^{13}C NMR spectrum exhibits signals of two differently coordinated cyclooctadiene ligands, as well as signals of free COD and sharp signals for CH_3OH and glycerol (Figure S5), all of which suggests an irreversible process [Equation (2), Scheme 2]. The two sets of signals can be attributed to dimeric Rh species containing one and two equivalents of diphosphane per Rh starting complex (compounds A and B, Scheme 2); the two observed differently coordinated COD ligands can be due to the different nature of the bridging alkoxide group.[16] Subsequent CO addition leads to the formation of two main species (Figure 2, bottom). One of them has non-equivalent P atoms [δ = 45.6 ppm (dd), J_{Rh-P} = 161.6 Hz, J_{P-P} = 43.7 Hz; 23.7 ppm (dd), J_{Rh-P} = 127.6 Hz, J_{P-P} = 43.7 Hz], which is consistent with monometallic Rh complexes coordinated to CO and BINAP (C, Scheme 2);[15] the other one exhibits a symmetrical environment, which leads to a unique doublet corresponding to a neutral species (δ = 46.9 ppm, J_{Rh-P} = 172 Hz) (D, Scheme 2). In the CO region, the ^{13}C NMR spectrum exhibits a doublet of doublets (δ =186.9 ppm, J_{Rh-CO} = 79.2 Hz, $J_{Ptrans-CO}$ = 17.8 Hz, $J_{Pcis-CO}$ = 2.5 Hz), which is in agreement with one CO ligand coordinated to the metal complex containing BINAP (Figure S6). Further addition of enynes (**1** or **2**) did not lead to the corresponding bicyclo[3.3.0]octenones (**1a** or **2a**), which shows that these saturated rhodium species are not able to coordinate the 1,6-enyne, which prevents the carbocyclisation because of the lack of enough labile positions around the metal centre. For $[Rh(\mu\text{-}Cl)(cod)]_2$, the same pattern of signals is observed after addition of *rac*-BINAP and CO (Figure S7).

However, Rh–TPPTS catalytic systems with monophosphane/Rh ratios lower than 2 lead to active species, as observed with TPPTS (Table 1, entry 9). For low TPPTS content, unsaturated Rh species stabilised by coordinated glycerol can be envisaged, which could be responsible for the catalytic activity, as proposed in Scheme S1.

The ^1H NMR monitoring of $[Rh(\mu\text{-}OMe)(cod)]_2$ in the presence of CO evidences the formation of both free COD and CH_3OH, which allows for the formation of cationic Rh

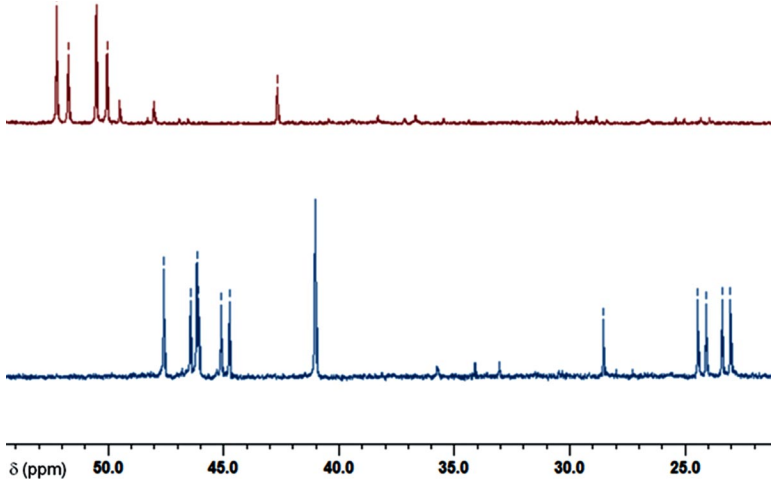
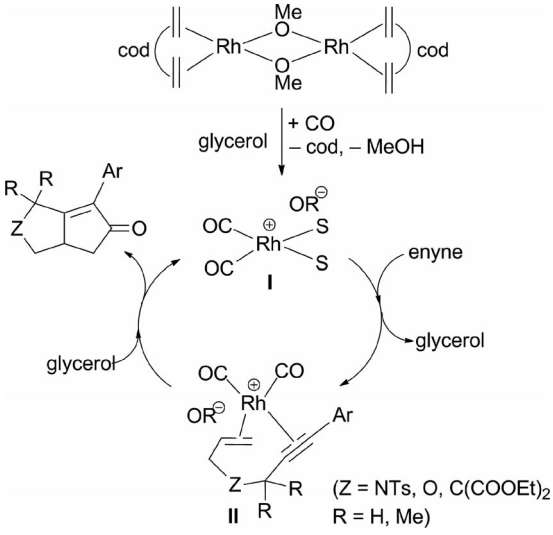


Figure 2. ^{31}P NMR spectra (121.5 MHz, CD_2Cl_2, 298 K) of $[Rh(\mu\text{-}OMe)(cod)]_2$ in glycerol after addition of *rac*-BINAP (top) and after subsequent addition of 1 bar CO (bottom). Rh/L/glycerol = 1:1:1. The signal at approximately 40 ppm is attributed to phosphane oxide.

species I (Scheme 3 and Figure S8), which favours a bidentate enyne coordination (species II in Scheme 3). The formation of bicyclo[3.3.0]octenone **2a** could be observed after addition of **2**. When [Rh(μ-Cl)(cod)]$_2$ was used under the same conditions, no COD decoordination was observed (Figure S8); the subsequent addition of enyne did not afford the Pauson–Khand product. Inactive species such as [RhCl(cod)(CO)] could probably be formed.



Scheme 3. Rh^{I} species proposed for the PKR catalysed by [Rh(μ-OMe)(cod)]$_2$ in glycerol under ligand-free conditions consistent with NMR studies (S = glycerol).

As stated above, the PKR also takes place in thf as coordinating solvent but with low selectivity (Table 1, entry 7), which is probably due to the robustness of the alkoxide group in this medium, which makes the bidentate coordination of the enyne difficult.[17]

Conclusions

In conclusion, we could demonstrate the feasibility of the Rh-catalysed PKR in glycerol, which shows that glycerol is stable and suffers neither decarbonylation nor dehydrogenation under catalytic conditions. Interestingly, ligand-free Rh systems are active and highly selective, depending on the nature of the organometallic precursor. Because of the Brønsted acid behaviour of glycerol, [Rh(μ-OMe)(cod)]$_2$, in contrast to [Rh(μ-Cl)(cod)]$_2$, catalyses the efficient formation of bicyclo[3.3.0]octenones. In this medium, the alkoxide groups are labile, favouring both the generation of vacant positions, which allows for enyne coordination, and the stabilisation of intermediates thanks to the coordinating behaviour of glycerol (Scheme 3), aspects required for the formation of the expected product. Further investigations concerning the use of glycerol in metal-catalysed processes are currently in progress.

Experimental Section

General: NMR spectra were recorded with a Bruker Avance 300 (300 MHz for ^{1}H NMR, 76.5 MHz for ^{13}C NMR, and 121.5 MHz for ^{31}P NMR spectra).

The 1,6-enynes *N*-allyl-*N*-(3-phenyl-2-propynyl)-4-tolylsulfonamide (**1**),[18] 3-allyloxy-1-phenylpropyne (**2**),[19] 3-allyloxy-1-(4′-methoxyphenyl)propyne (**5**),[20] and *N*-allyl-*N*-[3-(4′-methoxyphenyl)-2-propynyl]-4-tolylsulfonamide (**4**), and *N*-allyl-*N*-[3-(4′-nitrophenyl)-2-propynyl]-4-tolylsulfonamide (**6**)[21] were prepared as described in the literature. Diethyl allyl(3-phenyl-2-propynyl)malonate (**3**) was purchased from Alfa Aesar and used without further purification. Glycerol (99%, purchased from Sigma–Aldrich) was treated under vacuum at 80 °C overnight prior to use. The organic solvents were purified by standard procedures and distilled under nitrogen. [Rh(μ-Cl)(cod)]$_2$ was commercially available, and [Rh(μ-OMe)(cod)]$_2$ was prepared by following a reported methodology.[22]

Synthesis of Enyne 7

1-Iodo-4-nitrobenzene (1.24 g, 5 mmol), [PdCl$_2$(PPh$_3$)$_2$] (0.10 g, 3 mol-%), CuI (0.057 g, 6 mol-%), Et$_3$N (1.4 mL, 10 mmol), propargyl alcohol (0.302 mL, 5.2 mmol), and freshly distilled thf (5 mL) were introduced into a round-bottom flask with a Teflon inter-key under argon. The resulting dark-brown reaction mixture was stirred at 30–35 °C for 3 h (up to complete consumption of the iodo derivative, which was monitored by GC analysis). The product corresponding to the Sonogashira coupling was obtained as a light-brown solid after the evaporation of thf, and it was purified by flash column chromatography on silica gel by using dichloromethane as the eluent (0.8 g, 90% yield). ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 8.18 (d, J = 8.0 Hz, 2 H), 7.56 (d, J = 8.0 Hz, 2 H), 4.54 (s, 2 H), 2.08 (br. s, 1 H) ppm. ^{13}C NMR (CDCl$_3$, 76.4 MHz): δ = 147.4, 132.3, 129.6, 123.2, 92.6, 83.7, 51.4 ppm. MS (EI): m/z = 177.04.

3-(4-Nitrophenyl)-2-propyn-1-ol (0.7 g, 4 mmol), NaH (144 mg, 6 mmol), allyl bromide (0.17 mL, 6 mmol), and freshly distilled thf (10 mL) were mixed at room temperature for 18 h to give the corresponding enyne **7**. It was obtained as a light-yellow liquid after purification by flash column chromatography on silica gel with pentane/ethyl acetate (4:1) as the eluent (0.75 g, 86% yield). ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 8.18 (d, J = 8.0 Hz, 2 H), 7.59 (d, J = 8.0 Hz, 2 H), 5.89–6.00 (m, 1 H), 5.33 (dd, J = 17.0, 9.0 Hz, 2 H), 4.40 (s, 2 H), 4.15 (d, J = 5.0 Hz, 2 H) ppm. ^{13}C NMR (CDCl$_3$, 76.4 MHz): δ = 134.6, 132.4, 129.6, 123.5, 118.4, 90.7, 84.4, 85.3, 71.3, 57.8 ppm. MS (EI): m/z = 217.

Synthesis of Enyne 8

4-Iodoanisole (1.16 g, 5 mmol), [PdCl$_2$(PPh$_3$)$_2$] (0.10 g, 3 mol-%), CuI (0.057 g, 6 mol-%), Et$_3$N (1.4 mL, 10 mmol), 2-methyl-3-butyn-2-ol (0.503 mL, 5.2 mmol), and freshly distilled thf (5 mL) were introduced into a round-bottom flask with a Teflon inter-key under argon. The resulting dark-brown reaction mixture was stirred at 30–35 °C for 3 h (up to complete consumption of the iodo derivative, which was monitored by GC analysis). The product corresponding to the Sonogashira coupling was obtained as a light-brown solid after the evaporation of thf, and it was purified by flash column chromatography on silica gel by using dichloromethane as the eluent (0.84 g, 84% yield). ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.29 (d, J = 8.0 Hz, 2 H), 6.76 (d, J = 8.0 Hz, 2 H), 3.72 (s, 3 H), 1.53 (s, 6 H) ppm. ^{13}C NMR (CDCl$_3$, 76.4 MHz): δ = 159.7, 133.6, 115.5, 114.5, 92.5, 82.3, 65.6, 55.3, 31.6, 31 ppm. MS (EI): m/z = 190.11.

4-(4-methoxyphenyl)-2-methylbut-3-yn-2-ol (0.76 g, 4 mmol), NaH (144 mg, 6 mmol), allyl bromide (0.17 mL, 6 mmol), and freshly

distilled thf (10 mL) were mixed at room temperature for 18 h to give the corresponding enyne **8**. It was obtained as a light-yellow liquid after purification by flash column chromatography on silica gel by using pentane/ethyl acetate (5:1) as the eluent (0.85 g, 92% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.35–7.38 (d, J = 8.0 Hz, 2 H), 6.81–6.85 (d, J = 8.0 Hz, 2 H), 5.94–6.06 (m, 1 H), 5.35 (d, J = 17.0 Hz, 1 H), 5.14 (d, J = 10.0 Hz, 1 H), 4.19 (d, J = 5.0 Hz, 2 H), 3.79 (s, 3 H), 1.58 (s, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 76.4 MHz): δ = 159.6, 135.9, 133.1, 116.3, 114.8, 113.6, 89.9, 84.2, 71.1, 65.6, 55.4, 29.2 ppm. MS (EI): m/z = 230.10.

General Procedure for Rh-catalysed PKR: 0.0125 mmol [Rh(μ-X)(COD)]$_2$ (X = OMe: 6.05 mg; X = Cl^-, 6.05 mg) and, if appropriated, the corresponding ligand (0.025 mmol; TPPTS: 14.2 mg; *rac*-BINAP: 15.6 mg) were dissolved in glycerol (5 mL) in a Fisher–Porter bottle. The corresponding 1,6-enyne was then added (0.5 mmol; **1**: 162.5 mg; **2**: 86.11 mg), and the argon atmosphere was replaced by CO (0.5 bar). The mixture was then stirred at 80 °C for the desired time. After completion, CO was released in the hood, and extractions with dichloromethane were carried out (3× 10 mL). The organic phases were then concentrated under vacuum and analysed by ^{1}H NMR spectroscopy. The corresponding carbocyclisation product was isolated by following the reported procedure.[23]

2-(4-Nitrophenyl)-7-oxabicyclo[3.3.0]oct-1-en-3-one (7a): The product was obtained by a Rh-catalysed carbocyclisation from the enyne **7** by following the procedure described in the main text. The bicyclo[3.3.0]octenone **7a** was obtained as a colourless oil after purification by column chromatography on silica gel by using pentane/ethyl acetate (2:1) as the eluent. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.28- 7.74 (d, J = 16 Hz, 2 H), 7.74–7.71 (d, J = 8.0 Hz, 2 H), 5.04 (d, J = 16 Hz, 1 H), 4.67 (d, J = 8.0 Hz, 1 H), 4.34 (t, 1 H), 3.34 (m, 1 H), 3.2 (t, 1 H), 2.93 (dd, J = 6.0 Hz, 1 H), 2.4 (dd, J = 3.0 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 76.4 MHz): δ = 195.2, 149.2, 147.1, 138.7, 129.9, 127.3, 121.1, 75.6, 76.6, 38.7, 36.2 ppm. MS (EI): m/z = 245.13.

2-(4-Methoxyphenyl)-8,8-dimethyl-7-oxabicyclo[3.3.0]oct-1-en-3-one (8a): The product was obtained by a Rh-catalysed carbocyclisation from the enyne **8** by following the procedure described in the main text. The bicyclo[3.3.0]octenone **8a** was obtained as a yellow liquid after purification by column chromatography on silica gel by using pentane/ethyl acetate (2:1) as the eluent. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.23–7.26 (d, J = 8.0 Hz, 2 H), 6.92–6.95 (d, J = 8.0 Hz, 2 H), 4.34 (t, J = 8.0 Hz, 1 H), 3.83 (s, 1 H), 3.47–3.53 (m, 1 H), 3.38 (dd, J = 8.0, 11.0 Hz, 1 H), 2.80 (dd, J = 6.5, 17.5 Hz, 1 H), 2.31 (dd, J = 3.5, 18.0 Hz, 1 H), 1.65 (s, 3 H), 1.16 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 208.2, 183.2, 160.1, 135.3, 130.4, 123.1, 114.1, 78.9, 70.2, 55.5, 43.9, 39.2, 29.1, 24.1 ppm. MS (EI) m/z = 258.18.

Supporting Information (see footnote on the first page of this article): Additional NMR spectra (Figures S1–S8) and Scheme S1.

Acknowledgments

This work was financially supported by the Centre National de la Recherche Scientifique (CNRS) and the Université Paul Sabatier. F. C. thanks the Région Midi-Pyrénées and CNRS for a PhD grant. The authors thank Pierre Lavedan for the helpful NMR discussions.

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Received: May 22, 2013
Published Online: August 28, 2013

