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Sequential one-pot Rh(I)/Pd(0) catalysed cycloaddition–cyclisation–anion capture. Assembly of polyfunctional compounds

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Abstract

Wilkinson's catalyst and Pd(0) catalysts work harmoniously in sequence to create products containing three new rings, five or six bonds and one tetrasubstituted centre in ter- and tetramolecular processes. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Pd catalysis; Rh catalysis; cascade reaction; cycloaddition; cyclisation.

We have developed a wide range of powerful and selective Pd catalysed molecular queuing processes[1] whose potential would be considerably enhanced by interfacing with synthetically valuable catalytic processes mediated by other transition metals. Preliminary accounts of our electrochemically driven (Pd/Cr) Nozaki–Hiyama–Kishi reaction[2] and Heck-metathesis (Pd/Ru) reactions[3] have appeared and we now report versatile Rh/Pd processes.

We have previously developed a [2+2+2]-alkyne cycloaddition process catalysed by Wilkinson's catalyst [$(PPh_3)_3RhCl$].[4] To interface this process with our cyclisation–anion capture methodology (Scheme 1) requires identification of a common solvent for the Rh and Pd processes. Toluene has proved suitable for this combination of catalysts.

Ter- and tetramolecular processes have been evaluated using the common substrates **1**, **2** and **5** with a range of organotin, boron and hydride anion capture agents **Y** (Schemes 2 and 3).

A series of termolecular processes leading to **3** and **6** were evaluated first and the results are collected in Table 1.

A second series of tetramolecular processes were carried out on **1** and **5** in combination with **2**, CO (1 atm) and various anion capture agents **Y**. These are summarised in Table 2.

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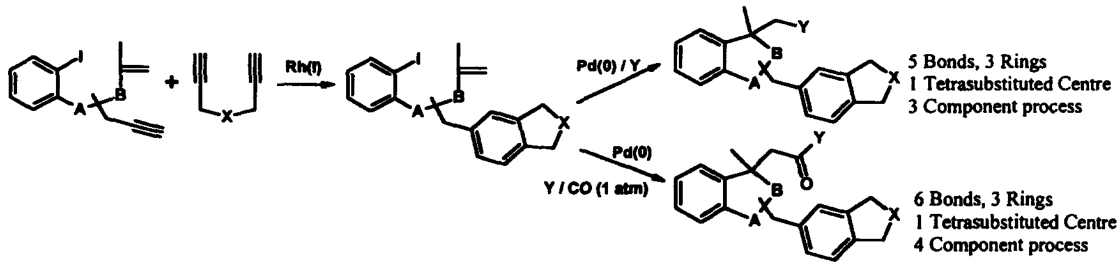
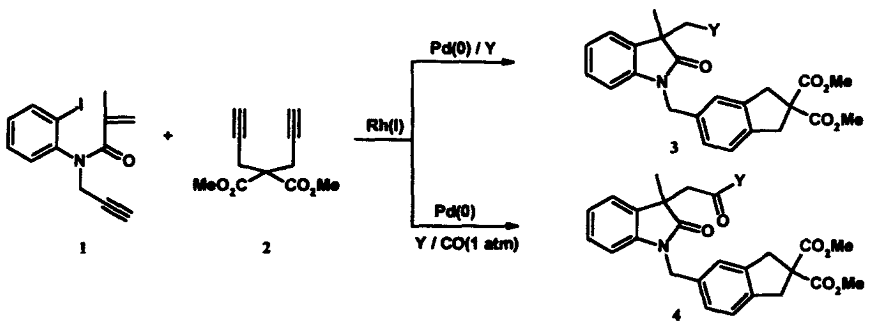
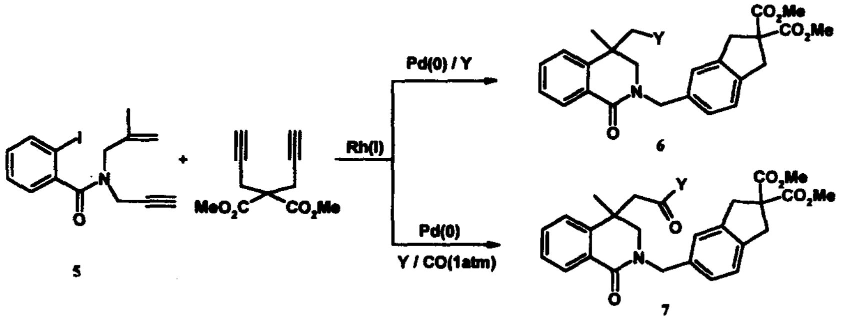


Scheme 1.



Scheme 2.



Scheme 3.

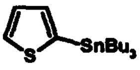
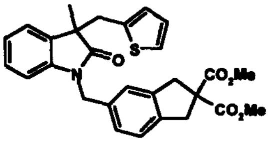
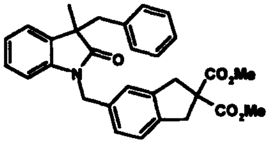
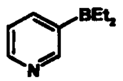
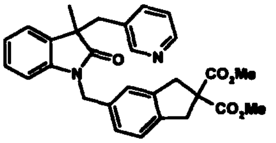
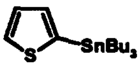
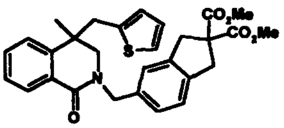
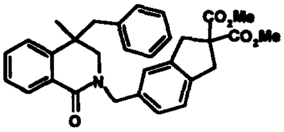
Two further reactions **1**→**8** (60%)→**9** (70%) and **5**→**10** (61%)→**11** (62%) each involving hydride capture have been performed in two steps and await further development into one-pot processes (Schemes 4 and 5).

It is clear that the Rh/Pd combination discussed herein offers a very effective enhancement of molecular complexity and that with appropriate variations of aryl iodide, 1,6-diyne and **Y** considerable molecular diversity can be created.

Acknowledgements

We thank Leeds University and the ORS for support.

Table 1
Termolecular Rh/Pd catalysed processes of **1** and **5**[a]

Aryl Iodide	Y	Additives	Temp (°C)[b]	Product	Yield (%)[c]
1		-	100		41
1	a. $NaBPh_4$ b. $PhB(OH)_2$	- -	Reflux Reflux		a. 54 b. 45
1		Na_2CO_3 (2eq) Et_4NCl (1eq)	110		49
5		-	110		39
5	$NaBPh_4$	-	Reflux		58

a. All reactions carried out in toluene initially at reflux for 4h with diyne **2** (1.5 mol eq.) and 5 mol% $(PPh_3)_3RhCl$. The mixture was then cooled to room temperature and Y (1 mol eq.), 10 mol% $Pd(OAc)_2$ and 20 mol% PPh_3, and appropriate additives added. Heating was then continued for 12-16 h.

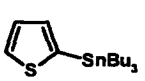
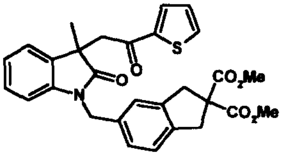
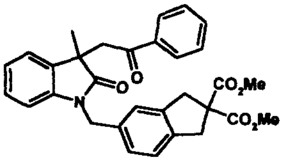
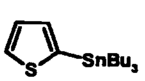
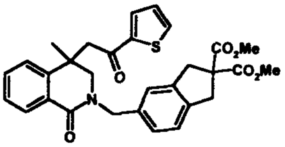
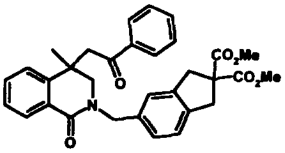
b. Oil bath temperature.

c. Isolated yields.

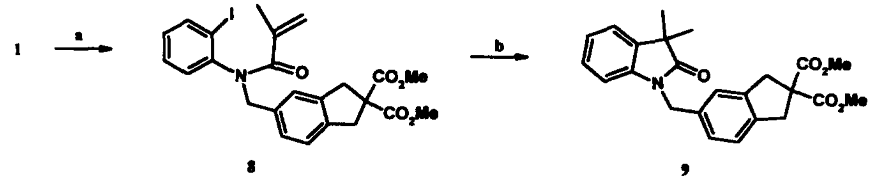
References

1. Grigg, R.; Sridharan, V. *J. Organomet. Chem.* **1999**, *576*, 65–87.
2. Grigg, R.; Putnikovic, B.; Urch, C. *Tetrahedron Lett.* **1997**, *35*, 6307–6308.
3. Grigg, R.; Sridharan, V.; York, M. *Tetrahedron Lett.* **1998**, *39*, 4139–4142; Evans, P.; Grigg, R.; Ramzan, M. I.; Sridharan, V.; York, M. *ibid.* **1999**, *40*, 3021-3024.
4. Grigg, R.; Scott, R.; Stevenson, P. *J Chem. Soc., Perkin Trans. 1* **1988**, 1357–1364; *idem., ibid.* **1988**, 1365–1369; Stevenson, P. J.; Neeson, S. J. *Tetrahedron Lett.* **1988**, *29*, 813–814; McDonald, F. E.; Zhu, H. Y. H.; Holmquist, C. R. *J. Am. Chem. Soc.* **1995**, *117*, 6605–6606.

Table 2
Tetramolecular Rh/Pd catalysed carbonylation processes of **1** and **5**[a]

Aryl Iodide	Y	Additives	Temp (°C)[b]	Product	Yield (%)[c]
1		-	90		45
1	$NaBPh_4$	Et_4NCl (1eq)	100		56
5		-	80		58
5	$NaBPh_4$	Et_4NCl (1eq)	100		41

a. Reaction conditions and times as for ***Table 1*** except that CO (1atm) was introduced *via* a balloon when the Pd catalyst was added.
b. Oil bath temperature.
c. Isolated yields.



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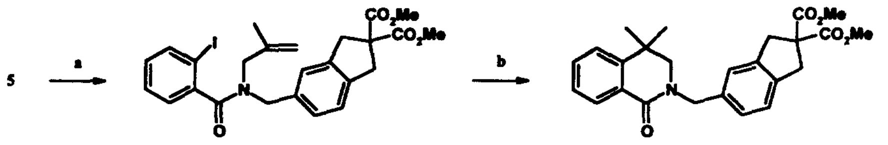
Scheme 4.



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Scheme 5. (a) Conditions as for Table 1. (b) HCO_2Na (1 mol equiv.) as hydride source, Et_4NCl (1 mol equiv.) and DMF as solvent (120°C, 12 h). Pd catalyst as for Table 1