DOI: 10.1002/adsc.201000408

Iridium(I)-Catalyzed Coupling of (*Z*)-2-En-4-yn-1-ols with Activated Alkynes: A New Synthetic Route to 7-Oxanorbornadienes

Alba E. Díaz-Álvarez,[a] Pascale Crochet,[a,*] and Victorio Cadierno[a,*]

[a] Departamento de Química Orgánica e Inorgánica, Instituto Universitario de Química Organometálica "Enrique Moles" (Unidad Asociada al CSIC), Universidad de Oviedo, Julián Clavería 8, 33006 Oviedo, Spain
Fax: (+34)-98-510-3446; e-mail: crochetpascale@uniovi.es or vcm@uniovi.es

Received: May 24, 2010; Revised: July 27, 2010; Published online: September 23, 2010

In memory of Prof. José Manuel Concellón who passed away in March 2010.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201000408.

Abstract: Taking advantage of the ability shown by the iridium(I) dimer [{Ir(μ-Cl)(COD)}$_2$] to promote the cycloisomerization of (*Z*)-enynols into furans, an unprecedented synthetic route to 7-oxanorbornadienes has been developed just by performing the catalytic reactions in the presence of activated alkynes. The process, which proceeds under solvent-free conditions, furnishes the bicyclic alkenes in good yields with complete atom-economy.

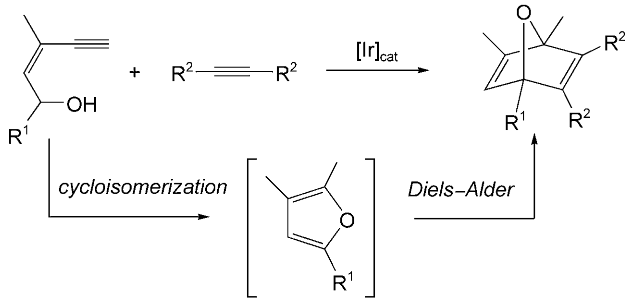
Keywords: bicyclic alkenes; cycloisomerization; Diels–Alder reaction; furans; iridium

The development of new methodologies aimed at improving efficiency is an important goal of contemporary organic synthesis. In particular, the replacement of multistep transformations by more straightforward "one-pot" processes is attracting considerable attention due to the obvious advantages of the latter, i.e., they minimize the overall reaction times, the generation of chemical waste and energy consumption, limiting therefore the global cost of the synthetic pathway.[1] In this context, transition metal catalysts provide an excellent tool for generating complex organic molecules, with high atom-economy,[2] from readily available starting materials via "one-pot" tandem processes.[3,4]

7-Oxabicyclo[2.2.1]hept-2,5-diene derivatives (7-oxanorbornadienes) represent a relevant class of compounds used as versatile synthetic intermediates in a huge number of cyclization, cycloaddition and coupling reactions,[5] as well as serving as monomers for functional polymers.[6] The traditional method for the construction of these oxabicyclic alkenes involves the Diels–Alder reaction of furans with activated alkynes.[5–7] However, the accessibility of furan skeletons with the desired substitution pattern is one of the most critical factors determining the applicability of the process in synthesis. In fact, the development of synthetic routes allowing the facile assembly of polysubstituted furans still remains an important objective for organic chemists.[8] Transition metal-catalyzed heteroannulation reactions of suitable acyclic precursors are probably the most appealing and innovative strategies to access furans since they usually proceed with complete atom-economy. Among the different acyclic substrates described to date in the literature,[8] (*Z*)-2-en-4-yn-1-ols are particularly attractive since they are readily available starting materials. In this context, several group 8–11 metal complexes have been successfully employed to promote the cycloisomerization of (*Z*)-2-en-4-yn-1-ols into the corresponding furans,[9] with ruthenium-, palladium- and gold-based catalysts showing the best performances.

Continuing with our interest in this type of cycloisomerization reaction,[9m–o] herein we would like to communicate that the commercially available iridium(I) dimer [{Ir(μ-Cl)(COD)}$_2$] (COD = 1,5-cyclooctadiene) is also a highly efficient and selective catalyst for the atom-economic conversion of (*Z*)-enynols into furans, representing a competitive alternative to the previously described Ru, Pd and Au systems. In addition, taking advantage of this, an unprecedented "one-pot" route to 7-oxanorbornadienes has also been developed just by performing the catalytic reactions in the presence of activated alkynes (Scheme 1).

Despite the prominent role that rhodium and iridium species play in homogeneous catalysis, their utility in the heteroannulation of (*Z*)-enynols still remains

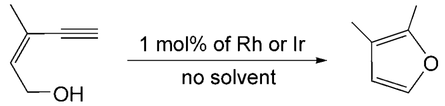


Scheme 1. One-pot synthesis of 7-oxanorbornadienes from (*Z*)-enynols and activated alkynes.

almost unexplored.[9h,m] That is why, using the cycloisomerization of (*Z*)-3-methyl-2-penten-4-yn-1-ol (**1a**) into 2,3-dimethylfuran (**2a**) as a model reaction, we decided to evaluate the efficiency and selectivity of several commercially available or readily accessible Rh and Ir precursors in this transformation. Initial experiments were performed at 80 °C, under solvent-free conditions, employing 5 mmol of **1a** and a metal loading of 1 mol% (see Table 1). Under these conditions (entries 1–8), all of the compounds tested led to the selective and almost quantitative formation of the desired furan **2a** in less than 1 h (≥96% GC yield). From this general catalyst screening, iridium clearly emerged as the metal of choice, with dimers [{Ir(μ-Cl)(COD)}$_2$] and [{Ir(μ-Cl)(COE)$_2$}$_2$] showing the best performances (>99% yield after only 10 min of heating; entries 7 and 8). Interestingly, both compounds were also able to promote the heteroannulation of **1a** at room temperature (entries 9 and 10). In particular, using [{Ir(μ-Cl)(COD)}$_2$] as catalyst, complete formation of **2a** could be reached after 3 h (entry 9). We note that, as far as we are aware, such a remarkable activity under mild conditions has only been previously described with palladium[9e,n] and gold catalysts,[9f,l,p,r] but never under solvent-free conditions.

Complex [{Ir(μ-Cl)(COD)}$_2$] was also effective in the selective cycloisomerization of a variety of other (*Z*)-enynols, thus confirming its potential for practical applications. As shown in Table 2, replacement of the hydrogen atom by alkyl (**1b**, **c**), aryl (**1d**, **e**) or alkenyl (**1f**, **g**) groups at C-1 of the 3-methyl-2-penten-4-yn-1-ol skeleton was compatible with the cyclization conditions, furans **2b–g** being selectively generated in excellent GC yields (≥97%) after 0.2–10 h of stirring at room temperature (entries 1–7). Alkynyl substituents at C-1 were also tolerated, i.e., (*Z*)-enynols **1h**, **i** (entries 8 and 9). However, in these cases the cycloisomerization process only takes place at 80 °C, the starting materials being recovered unchanged when the reactions were performed at room temperature for 24 h. Remarkably, the heteroannulation of (*Z*)-enynols **1j–l** bearing an internal C≡C bond was conveniently accomplished by [{Ir(μ-Cl)(COD)}$_2$] performing the catalytic reactions at 80 °C (entries 10–12), a reactivity to

Table 1. Comparison of different Rh and Ir catalysts in the cycloisomerization of (*Z*)-3-methyl-2-penten-4-yn-1-ol (**1a**) into 2,3-dimethylfuran (**2a**).[a]



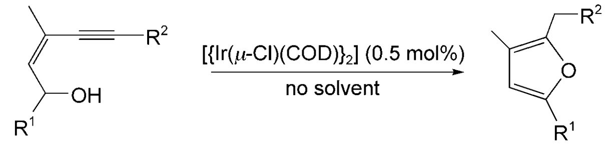
1a **2a**

Entry	Catalyst	*T* [°C]	*t* [min]	Yield [%][b]
1	[{Rh(μ-Cl)(COD)}$_2$]	80	50	>99
2	[{Rh(μ-Cl)(NBD)}$_2$]	80	20	>99
3	[{Rh(μ-Cl)(TFB)}$_2$]	80	20	>99
4	[{Rh(μ-Cl)(COE)$_2$}$_2$]	80	60	97
5	[{Rh(μ-Cl)(CO)$_2$}$_2$]	80	30	98
6	RhCl$_3$·*n* H$_2$O	80	60	96
7	[{Ir(μ-Cl)(COD)}$_2$]	80	10	>99
8	[{Ir(μ-Cl)(COE)$_2$}$_2$]	80	10	>99
9	[{Ir(μ-Cl)(COD)}$_2$]	r.t.	180	>99
10	[{Ir(μ-Cl)(COE)$_2$}$_2$]	r.t.	300	98

[a] Reactions performed under an N$_2$ atmosphere using 5 mmol of (*Z*)-methyl-2-penten-4-yn-1-ol (**1a**). [enynol]:[metal] ratio = 100:1. Abbreviations used: COD = 1,5-cyclooctadiene; NBD = norbornadiene; TFB = tetrafluorobenzobarralene; COE = cyclooctene.

[b] Determined by GC.

Table 2. Cycloisomerization of different (*Z*)-enynols catalyzed by [{Ir(μ-Cl)(COD)}$_2$].[a]



1a – k **2a – k**

Entry	Substrate (R^1/R^2)	*t* [h]	Product	Yield [%][c]
1	H/H (**1a**)	3	**2a**	>99 (87)
2	Et/H (**1b**)	0.2	**2b**	>99 (89)
3	*n*-Bu/H (**1c**)	0.2	**2c**	>99 (90)
4	Ph/H (**1d**)	6	**2d**	97 (81)
5	4-C$_6$H$_4$OMe/H (**1e**)	10	**2e**	98 (83)
6	CH$_2$CH=CH$_2$/H (**1f**)	2	**2f**	>99 (85)
7	CH$_2$C(Me)=CH$_2$/H (**1g**)	1	**2g**	>99 (87)
8[b]	C≡CSiMe$_3$/H (**1h**)	6	**2h**	92 (79)
9[b]	C≡CPh/H (**1i**)	1	**2i**	>99 (86)
10[b]	H/Ph (**1j**)	5	**2j**	83 (71)
11[b]	H/CH=CMe$_2$ (**1k**)	72	**2k**	93 (80)
12[b]	Et/Ph (**1l**)	4	**2l**	95 (81)

[a] Reactions performed at room temperature under N$_2$ atmosphere using 5 mmol of the corresponding (*Z*)-enynol **1a–l**. [enynol]:[Ir] ratio = 100:1.

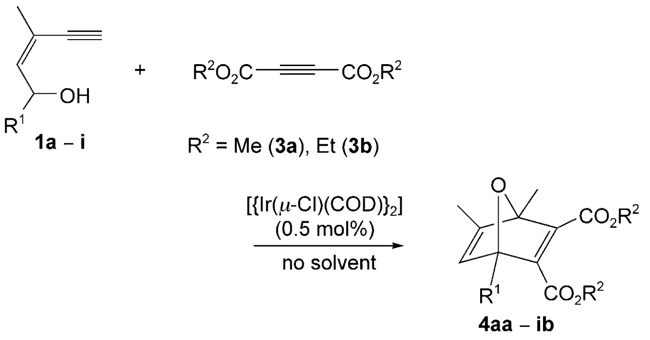
[b] Reaction performed at 80 °C.

[c] Determined by GC (isolated yield after appropriate work-up is given in brackets).

date restricted to palladium and gold catalysts, ruthenium and rhodium species being completely inoperative with internal alkynes.[9b,h] Purification of the crude reaction mixtures by bulb-to-bulb distillation (**2a–c**) or column chromatography on silica gel (**2d–l**) provided analytically pure samples of the furans which were isolated in 71–90% yield.

Interestingly, when these cycloisomerization processes were performed in the presence of a slight excess (1.3 equivalents) of the activated alkynes dimethyl acetylenedicarboxylate (**3a**) and diethyl acetylenedicarboxylate (**3b**) the clean formation of the corresponding 7-oxanorbornadiene derivatives was observed, *via* Diels–Alder cycloaddition between the *in situ* formed furan and the alkyne. We must note that, although the two individual transformations have been extensively studied, such a tandem cycloisomerization/cycloaddition process for the synthesis of 7-oxanorbornadienes is unprecedented. As shown in Table 3, with the exception of the alkynyl-substituted derivatives **4ia**, **ib** (entries 11 and 12), all reactions proceeded efficiently at room temperature furnishing the oxabicyclic alkenes in good isolated yields (60–88%) after appropriate chromatographic work-up. It is important to note that the two steps involved in this tandem process, i.e., the cycloisomerization reaction and the Diels–Alder cycloaddition, are promoted by the iridium catalyst. Effectively, when isolated 2,3-dimethylfuran (**2a**) was treated with dimethyl acetylenedicarboxylate (**3a**) in the absence of [{Ir(μ-Cl)(COD)}$_2$] no formation of **4aa** was observed at room temperature. Only on heating the mixture at 80 °C does the cycloaddition process occur.[10] We note that, to the best of our knowledge, participation of Ir(I) catalysts in Diels–Alder-type cycloadditions has not been yet quoted in the literature, the only examples reported involving Ir(III) derivatives.[11]

Table 3. Synthesis of 7-oxanorbornadienes by Ir-catalyzed coupling of (*Z*)-enynols with activated alkynes.[a]



Entry	(*Z*)-Enynol	Alkyne	*t* [h]	Product	Yield [%][c]
1	**1a**	**3a**	4	**4aa**	83
2	**1a**	**3b**	4	**4ab**	81
3	**1b**	**3a**	7	**4ba**	88
4	**1b**	**3b**	7	**4bb**	85
5	**1d**	**3a**	7	**4da**	88
6	**1d**	**3b**	9	**4db**	87
7	**1f**	**3a**	18	**4fa**	71
8	**1f**	**3b**	18	**4fb**	77
9	**1g**	**3a**	7	**4ga**	69
10	**1g**	**3b**	9	**4gb**	75
11[b]	**1i**	**3a**	2	**4ia**	60
12[b]	**1i**	**3b**	2	**4ib**	63

[a] Reactions performed at room temperature under an N_2 atmosphere using 5 mmol of the corresponding (*Z*)-enynol **1a–i** and 6.5 mmol of the appropriate alkyne **3a**, **b**. [enynol]:[alkyne]:[Ir] ratio = 100:130:1.

[b] Reaction performed at 80 °C.

[c] Isolated yield after chromatographic work-up.

In summary, a straightforward, operationally simple and highly efficient procedure for the preparation of 7-oxabicyclo[2.2.1]hept-2,5-diene derivatives from readily accessible (*Z*)-enynols and activated alkynes has been developed. The "one-pot" catalytic transformation presented herein, which represents a new example of the utility of iridium complexes in synthesis,[12] is based on an unprecedented tandem process consisting of the initial cycloisomerization of the (*Z*)-enynol into the corresponding furan and subsequent Diels–Alder cycloaddition of the latter with the alkyne. The overall process, which proceeds under solvent-free and remarkable mild conditions, represents an appealing synthetic route to this class of relevant oxabicyclic alkenes. We believe that the feasibility and scope of this atom-economical process (no by-products are generated) represent a competitive and very appealing methodology which could find applications in different synthetic programs in the near future. Further studies aimed at broadening the scope of this sequential catalytic process are currently in progress in our laboratory.

Experimental Section

General Procedure for the Catalytic Cycloisomerization of (Z)-Enynols into Furans

The corresponding (*Z*)-enynol **1** (5 mmol) and [{Ir(μ-Cl)(COD)}$_2$] (17 mg, 0.025 mmol) were introduced into a sealed tube under a nitrogen atmosphere. The resulting solution was then stirred at room temperature (**1a–g**), or heated at 80 °C in an oil bath (**1h–l**), for the indicated time (see Table 2; the course of the reaction was monitored by regular sampling and analysis by GC). The residue was then purified by bulb-to-bulb distillation (**1a–c**), or by column chromatography on silica gel (**1d–l**) using hexanes as eluent, to give furans **2**; yields: 71–90%. The identity of these compounds was assessed by comparison of their ^{1}H and ^{13}C{^{1}H} NMR spectral data with those previously described in the literature and by their fragmentation in GC/MSD analysis.

General Procedure for the Catalytic Synthesis of 7-Oxanorbornadienes from (*Z*)-Enynols and Alkynes

The corresponding (*Z*)-enynol **1** (5 mmol), the appropriate alkyne **3** (6.5 mmol) and $[\{Ir(\mu\text{-}Cl)(COD)\}_2]$ (17 mg, 0.025 mmol) were introduced into a sealed tube under a nitrogen atmosphere. The resulting solution was then stirred at room temperature (**1a, b, d, f, g**), or heated at 80 °C in an oil bath (**1i**), for the indicated time (see Table 3; the course of the reaction was monitored by regular sampling and analysis by TLC). The residue was then purified by column chromatography on silica gel, using a mixture of hexanes/diethyl ether (90:10) as eluent, to give 7-oxanorbornadienes **4**; yields: 60–88%. Characterization data, as well as copies of the ^{1}H and ^{13}C{^{1}H} NMR spectra, of all the bicycles synthesized can be found in the Supporting Information.

Acknowledgements

Financial support from the Spanish MICINN (Projects CTQ2006-08485/BQU and Consolider Ingenio 2010 CSD2007-00006) and the Gobierno del Principado de Asturias (FICYT Project IB08-036) is acknowledged.

References

[1] See, for example: a) L. F. Tietze, *Chem. Rev.* **1996**, *96*, 115–136; b) S. F. Mayer, W. Kroutil, K. Faber, *Chem. Soc. Rev.* **2001**, *30*, 332–339; c) J. M. Lee, Y. Na, H. Han, S. Chang, *Chem. Soc. Rev.* **2004**, *33*, 302–312.

[2] The concept of atom-economy has emerged as one of the major driving forces of modern chemistry: a) B. M. Trost, *Science* **1991**, *254*, 1471–1477; b) B. M. Trost, *Angew. Chem.* **1995**, *107*, 285–307; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 259–281; c) R. A. Sheldon, *Pure Appl. Chem.* **2000**, *72*, 1233–1246; d) B. M. Trost, *Acc. Chem. Res.* **2002**, *35*, 695–705; e) B. M. Trost, M. U. Frederiksen, M. T. Rudd, *Angew. Chem.* **2005**, *117*, 6788–6825; *Angew. Chem. Int. Ed.* **2005**, *44*, 6630–6666.

[3] See, for example: a) G. A. Molander, C. R. Harris, *Chem. Rev.* **1996**, *96*, 307–338; b) P. Eilbracht, L. Bärfacker, C. Buss, C. Hollmann, E. Kitsos-Rzychon, C. L. Kranemann, T. Rische, R. Roggenbuck, A. Schmidt, *Chem. Rev.* **1999**, *99*, 3329–3336; c) G. Poli, G. Giambastiani, A. Heumann, *Tetrahedron* **2000**, *56*, 5959–5989; d) S.-I. Ikeda, *Acc. Chem. Res.* **2000**, *33*, 511–519; e) J.-C. Wasilke, S. J. Obrey, R. T. Baker, G. C. Bazan, *Chem. Rev.* **2005**, *105*, 1001–1020; f) *Metal Catalyzed Cascade Reactions*, (Ed.: T. J. J. Müller), Springer Verlag, Berlin, **2006**.

[4] For a highly informative review on tandem catalysis, see: D. E. Fogg, E. N. dos Santos, *Coord. Chem. Rev.* **2004**, *248*, 2365–2379.

[5] For reviews, see: a) M. Lautens, W. Tam, *Adv. Met.-Org. Chem.* **1998**, *6*, 49–101; b) M. Lautens, K. Fagnou, S. Hiebert, *Acc. Chem. Res.* **2003**, *36*, 48–58; c) D. K. Rayabarapu, C.-H. Cheng, *Acc. Chem. Res.* **2007**, *40*, 971–983; d) W. Tam, N. Cockburn, *Synlett* **2010**, 1170–1189.

[6] See, for example: a) G. C. Bazan, J. H. Oskam, H.-N. Cho, L. Y. Park, R. R. Schrock, *J. Am. Chem. Soc.* **1991**, *113*, 6899–6907; b) J. G. Hamilton, J. J. Rooney, D. G. Snowden, *Makromol. Chem. Phys.* **1995**, *196*, 1031–1042; c) B. M. Novak, A. L. Safir, *Polym. Prepr.* **1996**, *37*, 335–336; d) M. R. Buchmeiser, G. K. Bonn, *PCT Int. Appl.* WO9827423, **1998**; e) L. Delaude, A. Demonceau, A. F. Noels, *Macromolecules* **1999**, *32*, 2091–2103; f) V. Amir-Ebrahimi, D. A. Corry, J. G. Hamilton, J. M. Thompson, J. J. Rooney, *Macromolecules* **2000**, *33*, 717–724; g) V. Amir-Ebrahimi, J. J. Rooney, *J. Mol. Catal. A: Chem.* **2004**, *212*, 107–113.

[7] See, for example: a) B. H. Lipshutz, *Chem. Rev.* **1986**, *86*, 795–819; b) F. Fringuelli, A. Taticchi, in: *The Diels–Alder Reaction: Selected Practical Methods*, John Wiley & Sons, West Sussex, **2002**; c) D. Heber, P. Rösner, W. Tochtermann, *Eur. J. Org. Chem.* **2005**, 4231–4247.

[8] For recent reviews, accounts, and highlights dealing with the synthesis of furans, see: a) X. L. Hou, H. Y. Cheung, T. Y. Hon, P. L. Kwan, T. H. Lo, S. Y. Tong, H. N. C. Wong, *Tetrahedron* **1998**, *54*, 1955–2020; b) B. A. Keay, *Chem. Soc. Rev.* **1999**, *28*, 209–215; c) A. Jeevanandam, A. Ghule, Y.-C. Ling, *Curr. Org. Chem.* **2002**, *6*, 841–864; d) R. C. D. Brown, *Angew. Chem.* **2005**, *117*, 872–874; *Angew. Chem. Int. Ed.* **2005**, *44*, 850–852; e) S. F. Kirsch, *Org. Biomol. Chem.* **2006**, *4*, 2076–2080; f) D. M. D'Souza, T. J. J. Müller, *Chem. Soc. Rev.* **2007**, *36*, 1095–1108; g) N. T. Patil, Y. Yamamoto, *ARKIVOC* **2007**, *10*, 121–141; h) G. Balme, D. Bouyssi, N. Monteiro, *Heterocycles* **2007**, *73*, 87–124; i) V. Cadierno, P. Crochet, *Curr. Org. Synth.* **2008**, *5*, 343–364; j) X.-L. Hou, Z. Yang, K.-S. Yeung, H. N. C. Wong, *Prog. Heterocycl. Chem.* **2009**, *21*, 179–223.

[9] For representative examples, see: a) D. Végh, P. Zalupsky, J. Kováč, *Synth. Commun.* **1990**, *20*, 1113–1123; b) B. Seiller, C. Bruneau, P. H. Dixneuf, *Tetrahedron* **1995**, *51*, 13089–13102; c) J. A. Marshall, C. A. Sehon, *J. Org. Chem.* **1995**, *60*, 5966–5968; d) B. Çetinkaya, I. Özdemir, C. Bruneau, P. H. Dixneuf, *J. Mol. Catal. A: Chem.* **1997**, *118*, L1–L4; e) B. Gabriele, G. Salerno, E. Lauria, *J. Org. Chem.* **1999**, *64*, 7687–7692; f) A. S. K. Hashmi, L. Schwarz, J.-H. Choi, T. M. Frost, *Angew. Chem.* **2000**, *112*, 2382–2385; *Angew. Chem. Int. Ed.* **2000**, *39*, 2285–2288; g) B. Çetinkaya, I. Özdemir, C. Bruneau, P. H. Dixneuf, *Eur. J. Inorg. Chem.* **2000**, 29–32; h) S. Elgafi, L. D. Field, B. A. Messerle, *J. Organomet. Chem.* **2000**, *607*, 97–104; i) P. Pale, J. Chuche, *Eur. J. Org. Chem.* **2000**, 1019–1025; j) I. Özdemir, B. Yiğit, B. Çetinkaya, D. Ülkü, M. N. Tahir, C. Arıcı, *J. Organomet. Chem.* **2001**, *633*, 27–32; k) B. Çetinkaya, N. Gürbüz, T. Seçkin, I. Özdemir, *J. Mol. Catal. A: Chem.* **2002**, *184*, 31–38; l) Y. Liu, F. Song, Z. Song, M. Liu, B. Yan, *Org. Lett.* **2005**, *7*, 5409–5412; m) A. E. Díaz-Álvarez, P. Crochet, M. Zablocka, C. Duhayon, V. Cadierno, J. Gimeno, J. P. Majoral, *Adv. Synth. Catal.* **2006**, *348*, 1671–1679; n) V. Cadierno, J. Díez, J. García-Álvarez, J. Gimeno, N. Nebra, J. Rubio-García, *Dalton Trans.* **2006**, 5593–5604; o) J. Albers, V. Cadier-

no, P. Crochet, S. E. García-Garrido, J. Gimeno, *J. Organomet. Chem.* **2007**, *692*, 5234–5244; p) X. Du, F. Song, Y. Lu, H. Chen, Y. Liu, *Tetrahedron* **2009**, *65*, 1839–1845; q) C. C. Schneider, H. Caldeira, B. M. Gay, D. F. Back, G. Zeni, *Org. Lett.* **2010**, *12*, 936–939; r) C. H. Oh, H. J. Yi, K. H. Lee, *Bull. Korean Chem. Soc.* **2010**, *31*, 683–688.

[10] In order to gain some insight on the role of iridium in the Diels–Alder cycloaddition step, the behaviour of [{Ir(μ-Cl)(COD)}$_2$] towards 2,3-dimethylfuran (**2a**) and dimethyl acetylenedicarboxylate (**3a**) was explored by means of ^{1}H NMR spectroscopy. Thus, we have found that, while [{Ir(μ-Cl)(COD)}$_2$] remains unchanged upon addition of an excess of **2a** in $CDCl_3$ at room temperature, it readily reacts, under the same conditions, with **3a** to afford a complicated mixture of products. Formation of only minor amounts of 7-oxanorbornadiene **4aa** was detected by ^{1}H NMR spectroscopy upon addition of **2a** to this mixture. This fact indicates that [{Ir(μ-Cl)(COD)}$_2$] is not the real active species in the final cycloaddition step. On the other hand, when a $CDCl_3$ solution of [{Ir(μ-Cl)(COD)}$_2$] was treated at room temperature with a mixture of (*Z*)-3-methyl-2-penten-4-yn-1-ol (**1a**) and dimethyl acetylenedicarboxylate (**3a**), the clean formation of **2a** was initially observed by ^{1}H NMR, evolving over time into **4aa**. Apparently, the active species of the Diels–Alder process is generated *in situ* from [{Ir(μ-Cl)(COD)}$_2$] and the (*Z*)-enynol during the initial cycloisomerization step.

[11] For recent examples, see: a) A. C. Atesin, J. Zhang, T. Vaidya, W. W. Brennsel, A. J. Frontier, R. Eisenberg, *Inorg. Chem.* **2010**, *49*, 4331–4342; b) D. Carmona, M. P. Lamata, F. Viguri, R. Rodríguez, C. Barba, F. J. Lahoz, M. L. Martín, L. A. Oro, L. Salvatella, *Organometallics* **2007**, *26*, 6493–6496; c) D. Carmona, M. P. Lamata, F. Viguri, R. Rodríguez, F. J. Lahoz, I. T. Dobrinovitch, L. A. Oro, *Dalton Trans.* **2007**, 1911–1921; d) D. Carmona, R. Medrano, I. T. Dobrinovitch, F. J. Lahoz, J. Ferrer, L. A. Oro, *J. Organomet. Chem.* **2006**, *691*, 5560–5566.

[12] *Iridium Complexes in Organic Synthesis*, (Eds.: L. A. Oro, C. Claver), Wiley-VCH, Weinheim, **2009**.