

New Platinum-Catalysed Dihydroalkoxylation of Allenes

María Paz Muñoz,^{a,*} María C. de la Torre,^a and Miguel A. Sierra^b^a Instituto de Química Orgánica General (IQOG), CSIC, Juan de la Cierva 3, 28006 Madrid, Spain

Fax: (+34)-91-564-4853; phone: (+34)-91-562-2900 ext: 437; e-mail: paz.munoz@iqog.csic.es

^b Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Avda. Complutense s/n, 28040 Madrid, Spain

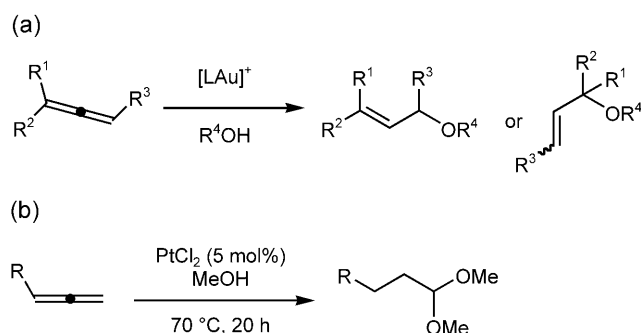
Received: May 3, 2010; Published online: September 7, 2010

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/adsc.201000342>.

Abstract: A new platinum-catalysed dihydroalkoxylation of allenes is described to give aliphatic acetals by an unexpected attack of two molecules of methanol to the terminal carbon of the allene moiety. Deuteration experiments suggest an unprecedented formal 1,3-dipolar addition of methanol to a zwitterionic platinum carbene as the key step. The first platinum-catalysed intermolecular carbon-based nucleophile addition to allenes is also reported.

Keywords: acetals; allenes; hydroalkoxylation; mechanism; platinum

Transition metal-catalysed hydroalkoxylation of allenes has received much attention in the last years, and both the intra-^[1] and intermolecular^[2] versions have been reported. For the intermolecular version, Au(I) complexes have proven to be the most active catalysts giving allylic ethers regioselectively by attack of the oxygen nucleophile to the terminal or internal carbon of the allenic system depending on the reaction conditions (Scheme 1, a).



Scheme 1. Au(I)- vs. Pt(II)-catalysed hydroalkoxylation of allenes.

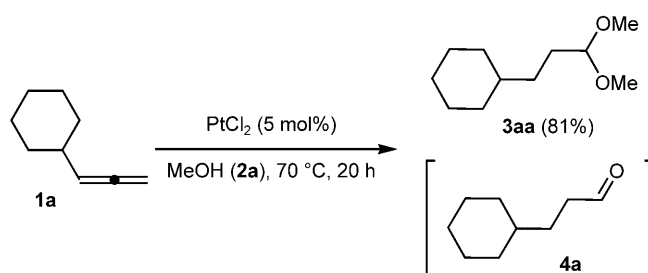
In the single example describing the formation of dimethyl acetals from allenes, the Au(I)-catalysed sequential addition of two molecules of methanol to the central carbon atom of allene is reported.^[3] However, to the best of our knowledge the double addition of *two molecules of MeOH* to the *terminal* carbon of an allene is unknown to date.

Here we report that the intermolecular reaction of allenes with alcohols in the presence of catalytic amounts of PtCl₂ follows a different reaction mode to the one reported for Au(I), leading to an unexpected aliphatic acetal formation by attack of two molecules of methanol to the terminal carbon of the allenic system and thus complete reduction of the allene is observed (Scheme 1, b).^[4]

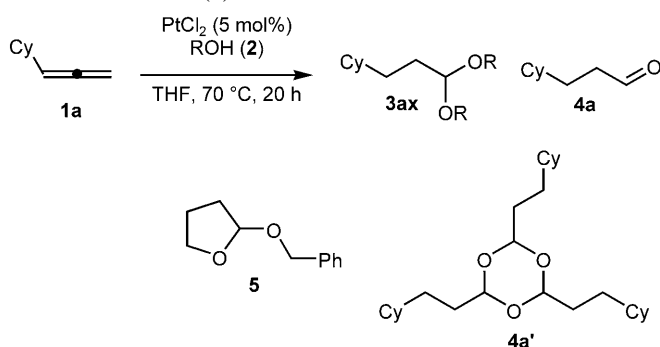
Commercially available cyclohexylallene **1a** was chosen as model substrate to study this reaction. Thus, heating **1a** in refluxing MeOH (**2a**) in the presence of 5 mol% of PtCl₂, led to the dimethyl acetal **3aa** in 81% along with traces of the corresponding aldehyde **4a**^[5] (Scheme 2).^[6]

Aldehyde **4a** could be obtained as the single reaction product when the reaction was carried out under similar conditions using a 3:1 mixture of THF:H₂O at 70 °C (Entry 1, Table 1).

The reaction was extended to the formation of different acetals by reaction of **1a** with other alcohols. The reactivity pattern for alcohols was found to be



Scheme 2. Pt-catalysed reaction of cyclohexylallene in MeOH.

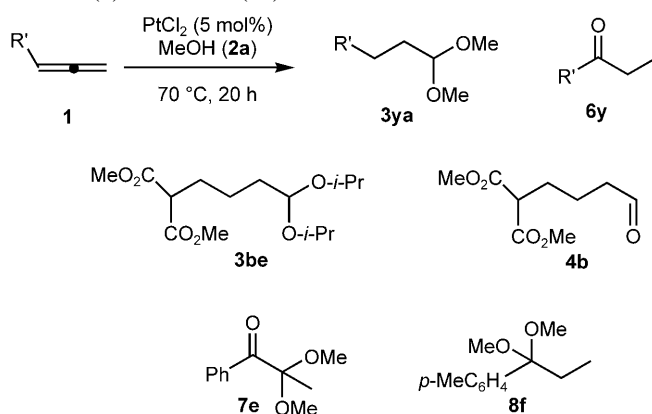
Table 1. Pt-catalysed reaction of cyclohexylallene (**1a**) and different alcohols (**2**).^[a]

Entry	2 , ROH (equiv.)	Products 3yx ^[b] (% isolated yield)
1	2b , H ₂ O	4a (67)
2	2c , EtOH ^[c]	3ac (49), 4a (18)
3	2d , <i>n</i> -BuOH ^[c]	3ad (61)
4	2e , <i>i</i> -PrOH ^[c]	4a' (75)
5	2f , <i>t</i> -BuOH ^[c]	4a (63)
6	2g , PhCH ₂ OH (3)	3ag (54), 5 ^[7] (34)
7	2h , OHCH ₂ CH ₂ CH ₂ OH (2)	3ah (75)

^[a] Reaction conditions: **1a** (0.2 mM), PtCl₂ (5 mol%), THF (2 mL), ROH (2–4 equiv.), 70 °C, 20 h. Conversion > 99%.

^[b] **3yx**: **y** refers to the allene and **x** to the alcohol used.

^[c] Neat alcohol, no THF used.

Table 2. Pt-catalysed reaction of different monosubstituted allenes (**1**) in MeOH (**2a**).^[a]

Entry	1 , Allenes	Products 3yx ^[b] (% isolated yield)
1	1b , R' = CH ₂ C(CO ₂ Me) ₂	3ba (85), 4b (15)
2	1b , R' = CH ₂ C(CO ₂ Me) ₂	3be (20) ^[c]
3	1c , R' = CH ₂ -phthalimide	3ca (78)
4	1d , R' = <i>n</i> -hexyl	3da (29), 6d (39)
5	1e , R' = Ph	3ea (61), 6e (21), 7e (5)
6	1f , R' = tolyl	3fa (32), 6f (30), 8f (2)

^[a] Reaction conditions: **1** (0.2 mM), PtCl₂ (5 mol%), MeOH (2 mL), 70 °C, 20 h. Conversion > 99%.

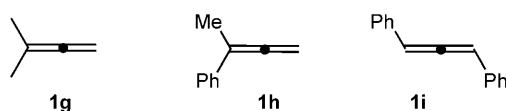
^[b] **3yx**: **y** refers to the allene and **x** to the alcohol used.

^[c] Reaction carried out in *i*-PrOH.

similar as in the Au-catalysed hydration of alkynes.^[3b] Results are shown in Table 1.

The hydroalkoxylation reaction is compatible with different types of alcohols. Primary alcohols, including EtOH, *n*-BuOH, secondary alcohols (*i*-PrOH), tertiary alcohols (*t*-BuOH), benzyl alcohol, and propane-1,2-diol all yielded the corresponding acetals **3ax**, together with variable amounts of free and trimeric aldehydes **4a** or **4a'**.^[8] The combined yield in aldehyde-derived compounds was good to excellent in the cases tested (Table 1). However, the use of alcohols having unsaturated motives (propargylic alcohol) rendered polymeric reaction mixtures, while phenol or acetic acid^[9] gave no reaction.^[10]

The substitution in the allene was next investigated using MeOH as the alcohol and PtCl₂ as the catalyst (Table 2 and Figure 1). Monosubstituted allenes^[11] formed the corresponding dimethyl acetals in moderate to good yields (entries 1 and 3–6, Table 2). In some cases (entries 4, 5, 6, Table 2), the ethyl ketone

**Figure 1.** Disubstituted allenes tested.

(**6y**) formed from the attack of methanol (or water) to the more substituted carbon of the allenic system was also obtained. The diisopropyl acetal **3be** could be isolated from the reaction of **1b** in *i*-PrOH without evidence of trimerization in this case (Entry 2, Table 2).

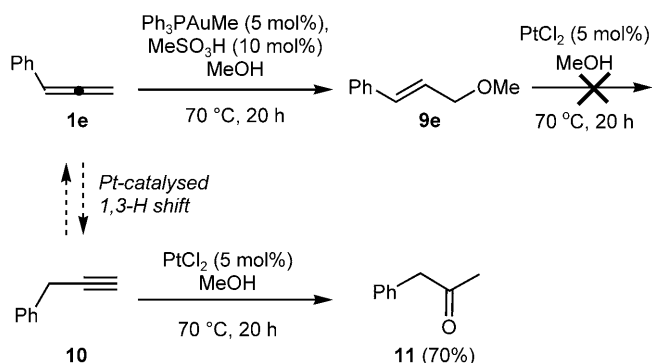
Results compiled in Table 2 show the compatibility of the dihydroalkoxylation of allenes with aliphatic, aromatic, esters and imide groups.^[12]

Opposite to monosubstituted allenes, disubstituted allenes yield no aliphatic acetals (Figure 1).^[13] Thus, geminal disubstituted allene **1g** led to decomposition, while **1h** formed traces of acetophenone under the same conditions (probably from a metathesis-like reaction). Similarly, 1,3-disubstituted allene **1i** gave a complex reaction mixture, from which no identifiable products could be isolated.

Although Au(I) and Pt(II) complexes often catalyse similar reactions, there are a few examples of divergent reactivity of these two metals.^[14] This seems to be the case of the reaction of simple allenes and alcohols. Thus, in the presence of Au(I) catalysts, allyl ethers are obtained *via* vinyl-Au intermediates,^[2] but in the presence of Pt(II) catalysts, terminal aliphatic acetals are produced.

To test the involvement of allyl ethers as intermediates in the formation of aliphatic acetals under our

Pt-catalysed conditions, the isolated allyl ether **9e** obtained from the reaction of **1e** in MeOH under Au(I)^[2c] catalysis, was then reacted with PtCl₂ under the conditions used in this work (Scheme 3). On the outset, **9e** was recovered unreacted and no acetal was detected, suggesting different reaction pathways in the reactions of allenes with each of these metals.



Scheme 3. Possible intermediates in the Pt(II)-catalysed reaction of allenes in MeOH.

The presence of discrete alkynes (arising from the isomerisation of the allene) as intermediates in this reaction was also ruled out^[15] by reaction of the commercially available 3-phenyl-1-propyne **10** under the same conditions, which led to ketone **11** in 70% yield as the only product (Scheme 3).

The formation of acetals may be explained through coordination of the Pt catalyst to the central carbon of the allene (**A**, Scheme 4), which can also be seen as a σ -allylic Pt cation (**B**, Scheme 4), and as a zwitter-

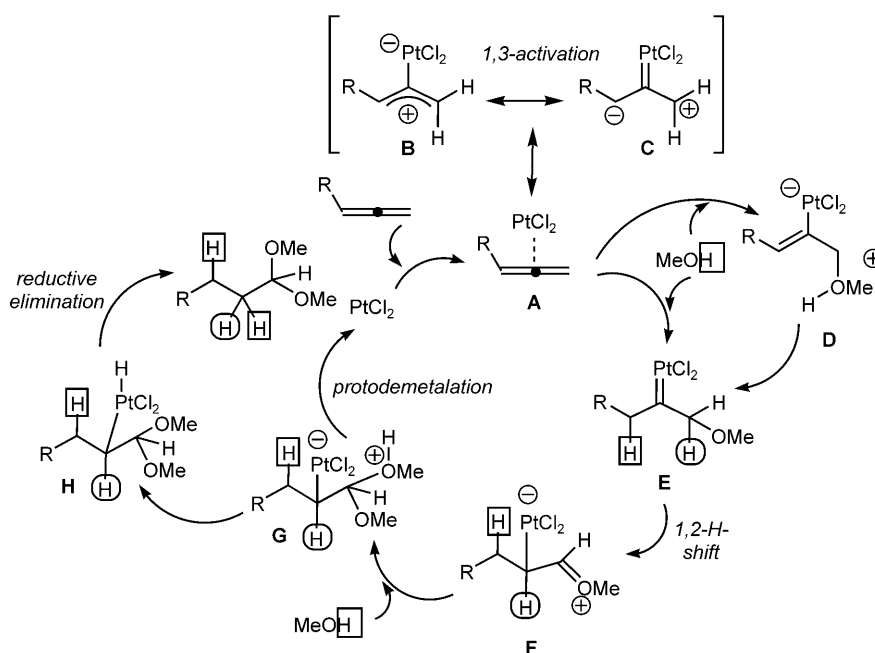
ionic Pt carbene^[16] or an all-carbon 1,3-dipole (**C**, Scheme 4).^[17,18] This Pt complex (**A** \leftrightarrow **B** \leftrightarrow **C**) would react with the alcohol in a 1,3-dipole manner or stepwise *via* a vinyl-Pt complex **D**, followed by protonation, to give Pt-carbene **E**. This new intermediate experiences a 1,2-H shift promoted by the highly electrophilic carbene carbon and the alkoxide moiety to yield intermediate **F**, which would lead to the final product by addition of a new alcohol molecule, followed by protodemetalation of **G**, or alternatively reductive elimination upon protonation of the metallic center (**H**, Scheme 4).^[19,20]

Proof to support this proposal was obtained by deuteration experiments. Thus, reaction of **1b** and **1e** with 5 mol% PtCl₂ in MeOD gave the corresponding 2,3-*d*₂-acetals with one deuterium added to the central carbon (from the final protodemetalation), and the other one to the internal more substituted carbon of the allenic system (from the first addition of MeOH) (Scheme 5).^[21,22]

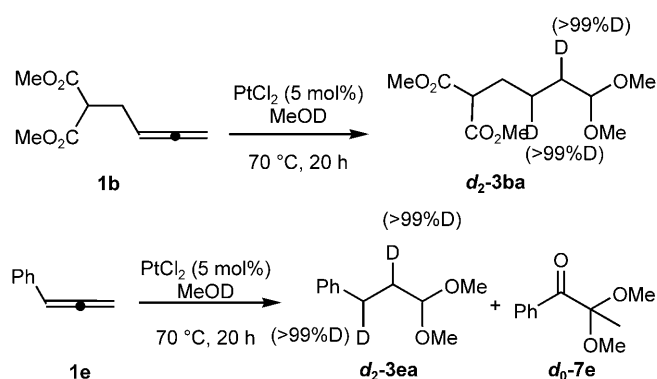
In our first attempt to extend this methodology to carbon-based nucleophiles,^[23] **3ai** was obtained as the only product, by a remarkable and unprecedented Pt-catalysed bis-indolization on the terminal carbon of **1a** (Scheme 6).^[24]

Although MeOH does not incorporate to the final product, it was essential to achieve high conversions, supporting a mechanism similar to the one proposed in Scheme 4, with the involvement of iminium intermediates of type **F'** (Scheme 6) stabilized in a more polar medium.^[25]

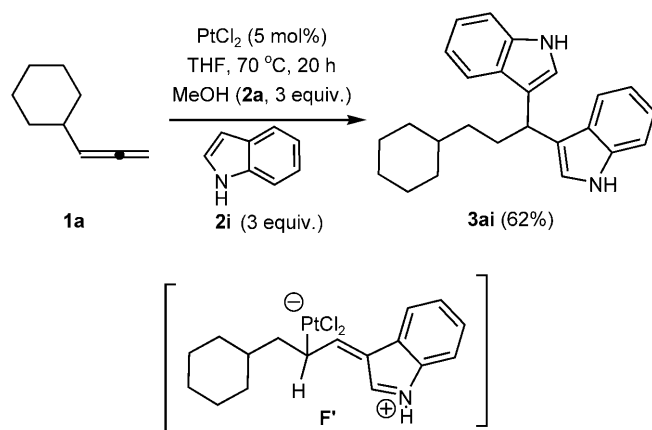
In conclusion, herein we describe a novel Pt-catalysed dihydroalkoxylation of allenes to give aliphatic acetals. The reaction showed an unprecedented and



Scheme 4. Proposed mechanism for the Pt-catalysed formation of acetals from allenes.



Scheme 5. Pt(II)-catalysed reaction of allenes in MeOD.



Scheme 6. Pt-catalysed reaction of cyclohexylallene **1a** with indole **2i**.

divergent reactivity compared to the Au(I)-catalysed version, and it is highly regioselective for the attack of two molecules of alcohol to the terminal carbon of the allenic system. Deuteration studies support the hypothesis of a zwitterionic Pt carbene as the key intermediate of this transformation. The key step could be seen as a formal 1,3-dipolar addition, with MeOH acting as the 1,3-dipole partner in a surprising and so far unreported behaviour. In addition, the first example of the intermolecular Pt-catalysed carbon-based nucleophiles addition to allenes has also been reported. Studies to extend this methodology to other carbon-based nucleophiles and to further understand this new reactivity mode are ongoing in our laboratory and will be reported in due course.

Experimental Section

General Procedure for Pt-Catalysed Dihydroalkoxylation of Allenes

A solution of allene (0.2–0.8 mmol) in dry THF (0.2 mM) or neat alcohol was added over PtCl₂ (5 mol%) under Ar. The

nucleophile (2–4 equiv.) was added when needed, and the reaction mixture heated at 70 °C for 20 h. The reaction was then cooled to room temperature and filtered through Celite. The solvent was evaporated and the crude purified by flash column chromatography on silica gel using hexane/Et₂O as eluent.

Acetal 3aa: colourless oil; yield: 80%. ¹H NMR (300 MHz, CDCl₃): δ = 4.29 (t, *J* = 5.7 Hz, 1 H), 3.27 (s, 6 H), 1.69–1.54 (m, 6 H), 1.21 (m, 6 H), 0.84 (m, 2 H); ¹³C NMR (75 MHz, CDCl₃): δ = 104.76, 52.39, 37.48, 33.23, 32.08, 29.76, 26.58, 26.28; HR-MS (ESI): *m/z* = 155.1428, calcd. for C₁₀H₁₉O (M⁺–OMe): 155.1430.

More details and characterization of all the products can be found in the Supporting Information.

Acknowledgements

The authors would like to thank the Spanish Government for a Ramón y Cajal Award to MPM. This work was supported by the Spanish Government (Consolider-Ingenio 2010: CSD2007-00006. MEC: CTQ2007-67730-C02-01/BQU) and the Comunidad Autónoma de Madrid (AVANCAT-CAM-S2009/PPQ-1634).

References

- [1] Au(III): a) A. Hoffmann-Röder, N. Krause, *Org. Lett.* **2001**, 3, 2537–2538; b) B. Gockel, N. Krause, *Org. Lett.* **2006**, 8, 4485–4488; c) C. Deutsch, B. Gockel, A. Hoffmann-Röder, N. Krause, *Synlett* **2007**, 1790–1794; d) J. Erdsak, N. Krause, *Synthesis* **2007**, 3741–3750; e) B. Alcaide, P. Almendros, T. Martínez del Campo, *Angew. Chem.* **2007**, 119, 6804–6807; *Angew. Chem. Int. Ed.* **2007**, 46, 6684–6687; Au(I): f) Z. Zhang, C. Liu, R. E. Kinder, X. Han, H. H. Qian, R. A. Widenhoefer, *J. Am. Chem. Soc.* **2006**, 128, 9066–9073; g) A. S. K. Hashmi, M. C. Blanco, D. Fischer, J. W. Batts, *Eur. J. Org. Chem.* **2006**, 1387–1389; h) Z. Zhang, R. A. Widenhoefer, *Angew. Chem.* **2007**, 119, 287–289; *Angew. Chem. Int. Ed.* **2007**, 46, 283–285; i) R. A. Widenhoefer, *Chem. Eur. J.* **2008**, 14, 5382–5391; Ln(III): j) X. Yu, S.-Y. Seo, T. J. Marks, *J. Am. Chem. Soc.* **2007**, 129, 7244–7245; Pd(II): k) R. D. Walkup, G. Park, *Tetrahedron Lett.* **1987**, 28, 1023–1026; Ag(I): l) L.-I. Olsson, A. Claesson, *Synthesis* **1979**, 743–745.
- [2] Au(I): a) N. Nishina, Y. Yamamoto, *Tetrahedron Lett.* **2008**, 49, 4908–4911; b) Z. Zhang, R. A. Widenhoefer, *Org. Lett.* **2008**, 10, 2079–2081; c) Z. Zhang, S. D. Lee, A. S. Fisher, R. A. Widenhoefer, *Tetrahedron* **2009**, 65, 1794–1798; d) N. Nishina, Y. Yamamoto, *Tetrahedron* **2009**, 65, 1799–1808; e) D.-M. Cui, K.-R. Yu, C. Zhang, *Synlett* **2009**, 1103–1106; for reaction of alkoxyallenes, see: f) D.-M. Cui, Z.-L. Zheng, C. Zhang, *J. Org. Chem.* **2009**, 74, 1426–1427; for a DFT study, see: g) R. S. Paton, F. Maseras, *Org. Lett.* **2009**, 11, 2237–2240; for different regiochemistry, see: h) M. S. Hadfield, A.-L. Lee, *Org. Lett.* **2010**, 12, 484–487; Pd: i) R. Zimmer, C. U. Dinesh, E. Nadanan, F. A. Khan, *Chem.*

- Rev. **2000**, *100*, 3067–3125, and references cited therein.
- [3] a) M. Schulz, J. H. Teles, (BASF AG), Patent WO-A1 9721648, **1997**; *Chem. Abstr.* **1997**, *127*, 121499; b) J. H. Teles, S. Brode, M. Chabanas, *Angew. Chem.* **1998**, *110*, 1475–1478; *Angew. Chem. Int. Ed.* **1998**, *37*, 1415–1417.
- [4] For reviews on Pt-catalysed reaction, see: a) M. Méndez, V. Mammann, A. Fürstner, *Chemtracts* **2003**, *16*, 397–425; b) A. M. Echavarren, C. Nevado, *Chem. Soc. Rev.* **2004**, *33*, 431–436; c) A. Fürstner, P. W. Davies, *Angew. Chem.* **2007**, *119*, 3478–3519; *Angew. Chem. Int. Ed.* **2007**, *46*, 3410–3449.
- [5] The aldehyde may be formed either by the hydrolysis of the acetal during purification by silica gel chromatography, or by nucleophilic attack of water, present in the methanol used, to the terminal carbon of the allene.
- [6] Reaction of **1a** in MeOH in the absence of Pt complex led to decomposition of the starting material. Reaction of **1a** with 5 mol% PtCl₂ in THF or toluene gave the allene recovered unreacted. Reaction at room temperature gave a 3:1 mixture of acetal **3aa** and allene **1a** after 24 h.
- [7] Compound **5** could be formed by the Pt-catalysed reaction of benzyl alcohol with the THF. Indeed, **5** was observed when benzyl alcohol was reacted in THF with a catalytic amount of PtCl₂ in the absence of the allene. For examples of this transformation with other catalysts, see: a) J. R. Falck, D. R. Li, R. Bejot, C. Mioskowski, *Tetrahedron Lett.* **2006**, *47*, 5111–5113; b) A. N. French, J. Cole, T. Wirth, *Synlett* **2004**, 2291–2294; c) M. Ochiai, T. Sueda, *Tetrahedron Lett.* **2004**, *45*, 3557–3559; d) J. M. Barks, B. C. Gilbert, A. F. Parsons, B. Upeandran, *Tetrahedron Lett.* **2000**, *41*, 6249–6252.
- [8] For catalytic trimerisation of enolisable aldehydes, see: a) Z. Zhu, J. H. Espenson, *Synthesis* **1998**, 417–422; b) Y.-S. Hon, C.-F. Lee, *Tetrahedron* **2001**, *57*, 6181–6188; c) B. Schetter, B. Ziemer, G. Schnakenburg, R. Mahrwald, *J. Org. Chem.* **2008**, *73*, 813–819.
- [9] For metal-catalysed hydrocarboxylation of allenes, see: Ir: a) I. S. Kim, M.-J. Krische, *Org. Lett.* **2008**, *10*, 513–515; Pd(0): b) N. T. Patil, N. K. Pahadi, Y. Yamamoto, *Can. J. Chem.* **2005**, *83*, 569–573.
- [10] Nitrogen (benzylamine) and sulfur-based nucleophiles (ethanedithiol) were not reactive under our reaction conditions. For an example of the intermolecular Au-catalysed hydroamination of allenes see Refs.^[2a,2c] For the Pd version, see: Ref.^[2] For the Rh version, see: A. H. Stoll, S. B. Blakey, *J. Am. Chem. Soc.* **2010**, *132*, 2108–2109.
- [11] Allenes **1b**, **1c**, **1d**, **1e**, **1f**, were prepared from the corresponding alkynes by Crabbé reaction or its microwave version: a) P. Crabbé, B. Nassim, M.-T. Robert-Lopes, *Org. Synth. Coll. Vol.* **7** **1990**, p 276; P. Crabbé, B. Nassim, M.-T. Robert-Lopes, *Org. Synth.*, Vol. 63, **1985**, p 203; b) H. Nakamura, T. Sugiishi, Y. Tanaka, *Tetrahedron Lett.* **2008**, *49*, 7230–7233.
- [12] The intramolecular version of the Pt-catalysed hydroalkoxylation reaction was also explored using hydroxyallenes, but mostly polymeric mixtures were obtained. See Supporting Information for details. Hydroxyallenes have shown to give hydrofurans or benzofulvenes in the reaction with Au(I): a) A. Hoffmann-Röder, N. Krause, *Org. Lett.* **2001**, *3*, 2537–2538; b) A. S. K. Hashmi, M. C. Blanco, D. Fischer, J. W. Bats, *Eur. J. Org. Chem.* **2006**, 1387–1389; c) P. Cordier, C. Aubert, M. Malacria, E. Lacôte, V. Gandon, *Angew. Chem.* **2009**, *121*, 8913–8916; *Angew. Chem. Int. Ed.* **2009**, *48*, 8757–8760.
- [13] Allene **1g** is commercially available (Aldrich) and was used without further purification. Allene **1h** was prepared from the corresponding propargyl alcohol by reduction with AlH₃: A. Claesson, L.-I. Olsson, *J. Am. Chem. Soc.* **1979**, *101*, 7302–7311. Allene **1i** was prepared using a modified Crabbé reaction: J. Kuang, S. Ma, *J. Am. Chem. Soc.* **2010**, *132*, 1786–1787.
- [14] For some examples see: a) A. S. K. Hashmi, E. Kurpejovic, W. Frey, J. W. Bats, *Tetrahedron* **2007**, *63*, 5879–5885; b) L. Zhang, *J. Am. Chem. Soc.* **2005**, *127*, 16804–16805; c) G. Zhang, V. J. Catalano, L. Zhang, *J. Am. Chem. Soc.* **2007**, *129*, 11358–11359.
- [15] For an example of double methanol addition in a very unusual *anti*-Markovnikov manner to an alkyne in the PtCl₂-catalysed reaction of allenynes in MeOH, see: T. Matsuda, S. Kadowaki, M. Murakami, *Helv. Chim. Acta* **2006**, *89*, 1672–1680.
- [16] For Au(I) examples, see: a) J. H. Lee, F. D. Toste, *Angew. Chem.* **2007**, *119*, 930–932; *Angew. Chem. Int. Ed.* **2007**, *46*, 912–914; b) D. Benítez, E. Tkatchouk, A. Z. González, W. A. Goddard III, F. D. Toste, *Org. Lett.* **2009**, *11*, 4798–4801; c) P. Mauleón, R. M. Zeldin, A. Z. González, F. D. Toste, *J. Am. Chem. Soc.* **2009**, *131*, 6348–6349; d) B. Trillo, F. López, S. Montserrat, G. Ujaque, L. Castedo, A. Lledós, J. L. Mascareñas, *Chem. Eur. J.* **2009**, *15*, 3336–3339. For Pt(II) examples, see: e) H. Funami, H. Kusama, N. Iwasawa, *Angew. Chem.* **2007**, *119*, 927–929; *Angew. Chem. Int. Ed.* **2007**, *46*, 909–911; f) B. Trillo, F. López, M. Gullías, L. Castedo, J. L. Mascareñas, *Angew. Chem.* **2008**, *120*, 965–968; *Angew. Chem. Int. Ed.* **2008**, *47*, 951–954; g) W. Kong, C. Fu, S. Ma, *Chem. Commun.* **2009**, 4572–4574.
- [17] For examples of 1,3-dipolar cycloaddition using all-carbon Au and Pt 1,3-dipoles, see: a) X. Huang, L. Zhang, *J. Am. Chem. Soc.* **2007**, *129*, 6398–6399; b) Ref.^[14c]
- [18] Several structures have been proposed for the coordination of a metal to an allene, the most common being a η^2 -complex involving one of the two double bonds. However, coordination of the metal only to the central carbon has also been proposed, being the σ -allylic metal cation the model most used to explain reactivity. This cation can also be seen as a zwitterionic carbene or an all-carbon 1,3-dipole as proposed in Scheme 4. For reviews on transition metal-allene complexes, see: a) T. L. Jacobs, in: *The Chemistry of the Allenes*, Vol. 2, (Ed.: S. R. Landor), Academic Press, London, **1982**, pp 277; b) V. Gandon, G. Lemièrre, A. Hours, L. Fensterbank, M. Malacria, *Angew. Chem.* **2008**, *120*, 7644–7648; *Angew. Chem. Int. Ed.* **2008**, *47*, 7534–7538, and references cited therein.
- [19] Styrene was reacted with **1a** in the presence of MeOH to trap carbene intermediate **E** in an alternative path-

way to the 1,2-H migration. However, only dimethyl acetal **3aa** was obtained (80%). For intermolecular trapping of Pt-carbene intermediates, see: B Martín-Matute, C. Nevado, D. J. Cárdenas, A. M. Echavarren, *J. Am. Chem. Soc.* **2003**, *125*, 5757–5766.

- [20] A mechanism involving vinyl ethers as intermediates was also investigated and cannot be completely ruled out. However, the reaction of **1e** and 1 equiv. of MeOH in THF gave only unreacted starting material and no vinyl ether or other intermediate was detected.
- [21] A mechanism involving Pt–H cannot be completely ruled out. However, if this species gave scrambling with MeOD, the observed complete deuterium incorporation in the final products would not be explained.
- [22] Formation of ketones **6y** could be explained by the reverse regioselectivity of the MeOH 1,3-addition or by allene-alkyne isomerisation by 1,3-H migration to form the internal alkyne, followed by hydration with traces of water. This second hypothesis would be more probable due to the lack of ketone formation in the presence of drier MeOD. Formation of **7e** is currently being investigated.
- [23] For the only example of intermolecular Au(I)-hydroarylation of allenes to give *E*-allylated products, see: M. A. Tarselli, A. Liu, M. R. Gagné, *Tetrahedron* **2009**, *65*, 1785–1789. For an intramolecular example, see: Ref.^[14] For Mn-catalysed allylation of allenes, see: T. Nishikawa, H. Shinokubo, K. Oshima, *Org. Lett.* **2003**, *5*, 4623–4626.
- [24] For a Pt-catalysed reaction of allenols in the presence of indoles, see: W. Kong, J. Cui, Y. Yu, G. Chen, C. Fu, S. Ma, *Org. Lett.* **2009**, *11*, 1213–1216. For synthesis of β,β -bisindolyl ketones by Sc-catalysed reaction of allenyl ketones and indoles, see: S. Ma, S. Yu *Org. Lett.* **2005**, *7*, 5063–5065.
- [25] Reaction in MeOD, gave **3ai** in 60% with no deuterium incorporation. Reaction of **1a** and 3 equivalents of indole **2i** in THF under the same conditions with no MeOH added, gave low conversion of the allene and **3ai** was obtained in only 23%.