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EMERGING AREA

Transition metal-catalysed (4 + 3) cycloaddition reactions involving allyl cations

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In this *emerging area* article, we focus on novel intramolecular transition metal catalysed (4 + 3)-cycloaddition reactions of allenedienes in which the allene acts as an allylic-cation surrogate. This process has emerged as a powerful tool for the construction not only of complex seven-membered rings containing compounds but also different types of useful molecular skeletons by the proper selection of the catalyst. The transformation proceeds with high chemo- and stereoselectivity mainly because it occurs through an *exo*-like concerted transition state which exhibits a clear *in-plane* aromatic character. Despite that, different reaction mechanisms (*i.e.* stepwise processes) are also possible depending on the nucleophilicity of the diene moiety.

1. Introduction

Since the first report by Fort in 1962 describing the preparation of an 8-oxabicyclo[3.2.1]oct-6-en-3-one derivative (Scheme 1),[1] the (4 + 3)-cycloaddition reaction involving allyl cations has emerged as a quite convenient way to produce relatively complex seven-membered rings from simple starting materials.[2] This pericyclic reaction, which has been successfully applied to the synthesis of complex natural products containing seven-membered rings,[2] continues to be investigated and is nowadays a topic of renewed interest, as nicely summarized by Harmata in two consecutive review articles which have been published quite recently.[3]

Despite the usefulness of this transformation, the standard methodologies used (which mainly involve oxy- and amino-allyl

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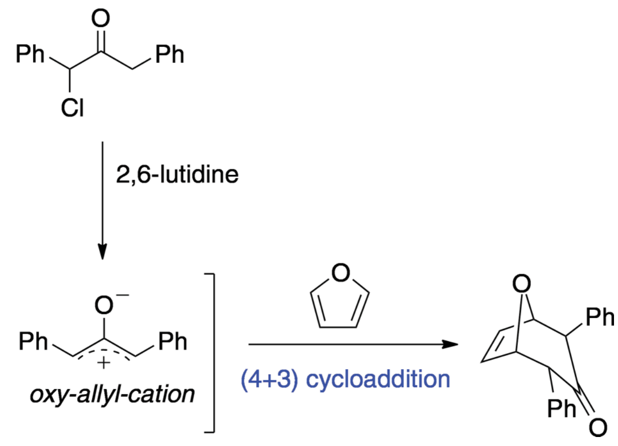


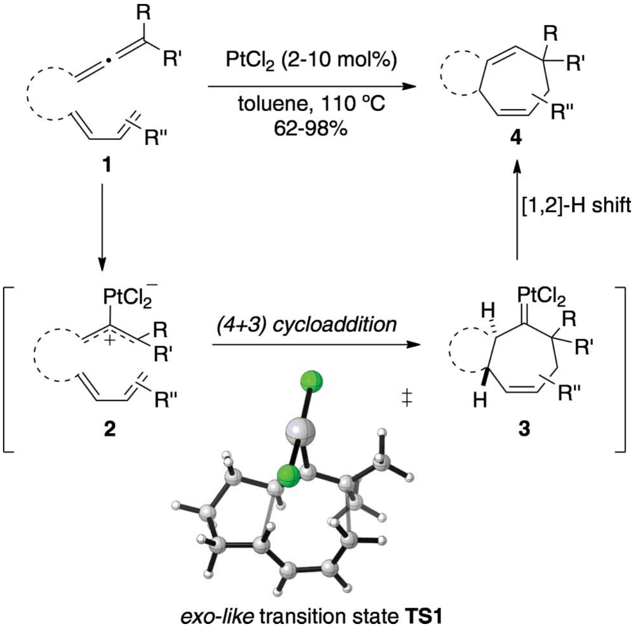
Scheme 1 First (4 + 3) cycloaddition reaction involving an oxy-allyl cation reported by Fort.[1]

cations) usually present important limitations, *i.e.* unstable allyl cation precursors or the need for stoichiometric activators,[4] and the requirement of conformationally restricted dienes (furans or cyclopentadienes). To avoid these shortcomings, new cycloaddition reactions involving transition metal catalysts have been described recently.[5] In the present *emerging area* article, we shall focus on such transformations, which are quite attractive not only due to their tremendous potential in organic synthesis but also due to their intricacies, *i.e.* reaction mechanisms and aromaticity of the involved transition states.

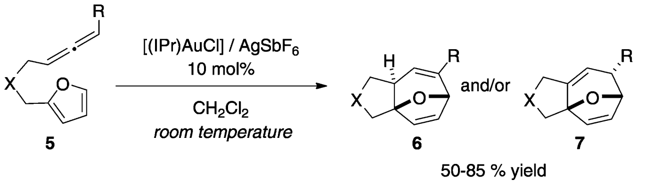
2. (4 + 3)-Cycloaddition reactions mediated by platinum(II) and gold(I) complexes

Very recently, Mascareñas and co-workers reported that $PtCl_2$ can catalyse the diastereoselective transformation of allene-tethered 1,3-dienes **1** into the synthetically useful bicyclo [5.3.0]decane skeletons **4** (Scheme 2).[6] This method provides a straightforward and atom economical entry to a variety of cycloheptene-containing polycycles from readily available acyclic allenediene precursors, which tolerates different substituents in both the allene and the diene moieties. By a combination of experimental and computational (DFT, B3LYP/6-31G(d) and LanL2DZ level) methodologies, it has been suggested that the reaction first involves a π-activation of the allene moiety by the metal catalyst to give rise to a metal-allyl cation intermediate **2** which undergoes a concerted (4 + 3)-cycloaddition reaction to produce the cycloheptenyl metal–carbene **3** (Scheme 2). This transformation occurs through the *exo*-like transition state **TS1**, which explains the perfect diastereoselectivity of the process towards the formation of *trans*-fused cycloadducts. A subsequent 1,2-hydrogen shift on the resulting metal–carbene **3** yields the final [4C+3C] adduct and regenerates the catalyst.

Similarly, gold(I) salts containing a σ-donating N-heterocyclic carbene (NHC) ligand also promote the above described (4 + 3)-cycloaddition-1,2-H shift sequence.[7] These reactions can be performed with a greater variety of dienes, including furans, therefore increasing the scope and synthetic utility of the process, and interestingly, at lower temperatures (Scheme 3). According to DFT calculations, this is mainly due to the lower activation barrier of the 1,2-H shift process.[7]



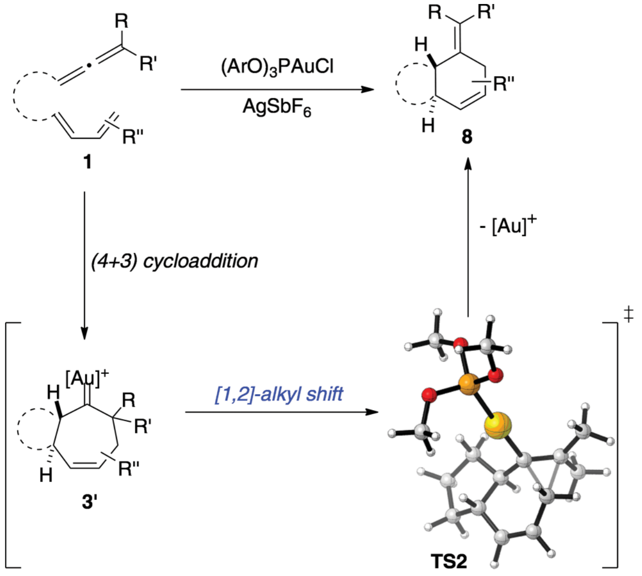
Scheme 2 Pt(II)-catalysed (4 + 3)-cycloaddition reaction of allenedienes.



Scheme 3 Gold(I)-NHC catalysed (4 + 3)-cycloaddition reaction of allenes **5**.

The above results suggest that the cycloaddition is sensitive to modifications on the transition metal and its ligands. For this reason, it is not surprising that the outcome of the process may change when ligands with different electronic and/or steric properties are used. Thus, whereas σ-donor NHC or biphenyl-di-*tert*-butyl phosphine ligands at gold provide selectively (4 + 3)-adducts,[8,9] π-acceptor triarylphosphites promote formal (4 + 2)-annulations to give *trans*-fused bicyclic cycloadducts **8**. Current data suggest that the formation of these products involve a ring contraction on the corresponding metal–carbene complex **3′** (Scheme 4).[8,10,11] Strikingly, a chemoselective and highly enantioselective process can be achieved using chiral phosphoramidite-based Au(I) complexes.[10a]

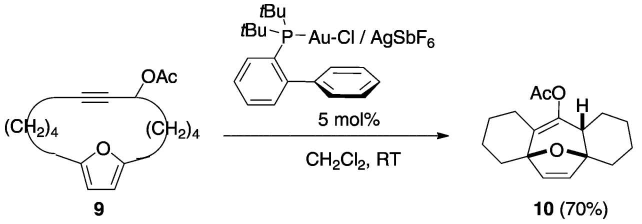
DFT calculations (PCM-B3LYP/6-311++G(d,p) and LanL2DZ//B3LYP/6-31G(d) and LanL2DZ level) confirm that with phosphite ligands the 1,2-H shift (which would lead to a reaction product similar to **4**, Scheme 2) is disfavoured with respect to the 1,2-alkyl migration, a transformation that produces the (4C + 2C) cycloadduct **8** *via* the saddle point **TS2** (Scheme 4).[10a] This suggests that the formation of products **4** and **8** has the same origin, *i.e.* the concerted (4 + 3)-cycloaddition from the corresponding metal-allyl cation intermediate. Depending on the stereoelectronic properties of the ligand at gold and the relative strength of the dπ to pπ interaction in the Au–C bond, this intermediate might evolve by 1,2-H shift or by ring contraction.[11] Similar types of dichotomies (control of the allene moiety behaviour as 2C or 3C component in the annulation



Scheme 4 A formal (4 + 2)-process originated from a previous (4 + 3)-allenediene cycloaddition reaction.

to alkenes depending on the electronic and steric properties of gold catalysts) have been described by the groups of Toste[12] and Fürstner[13] as well.

The enormous potential of this metal-mediated cycloaddition reaction involving allyl-cations is clearly illustrated by the transannular version of the (4 + 3)-process reported by Gung and co-workers.[14] As shown in Scheme 5, propargyl acetate **9**, which is formally acting as an allene surrogate, is easily transformed into the complex compound **10** upon exposure to the bulky biphenyl-di-*tert*-butyl phosphine gold(I) catalyst. This transformation allows the rapid construction of the tetracyclic core of Cortistatin A, a potent antiangiogenesis natural product.[15] As expected, the outcome of the reaction was found to be strongly dependent on the gold catalyst employed.[14]



Scheme 5 Gold(I)-catalysed transannular (4 + 3)-cycloaddition reaction.

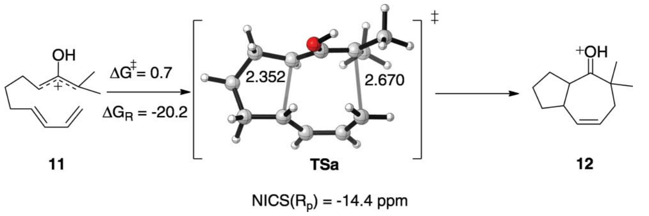
3. Intricacies of the metal-mediated (4 + 3)-cycloaddition process

The above findings nicely confirm that the transition metal catalysed (4 + 3)-cycloaddition reaction is a powerful tool for easy and stereocontrolled access to complex seven-membered rings containing compounds. Furthermore, the intricacies of this cycloaddition are equally interesting from a fundamental point of view. Issues such as the aromaticity of the corresponding seven-membered concerted transition states and the detailed study of the reaction mechanisms depending on the involved transition metal and diene moieties are discussed in this section.

3.1. Aromaticity in the (4 + 3)-cycloaddition

The parent (4 + 3)-cycloaddition reaction between an oxy-allyl cation and a diene (Scheme 1) involves the circulation of six electrons in a cyclic array. This situation resembles that of different pericyclic processes such as Diels–Alder or double-group transfer reactions which also involve the movement of 4*n* + 2 electrons in closed circuits, thus satisfying the Hückel rule for aromaticity.

The highly negative Nuclear Independent Chemical Shift[16] (NICS = −14.4 ppm) value computed at the (3,+1) ring critical point of the electron density[17] of the transition state **TSa** for the reaction depicted in Scheme 6, confirms the aromatic character of this saddle point.[18] Therefore, it can be proposed that the six electrons involved in the cycloaddition lie approximately in the molecular plane and give rise to an appreciable ring current which in turn, promotes a strong diamagnetic shielding at the ring critical point, leading to the observed negative NICS value. This special type of aromaticity belongs to the so-called *in-plane* aromaticity and can be found in many other pericyclic reactions.[19] Moreover, the delocalization of electrons which are responsible for the aromaticity can be visualized with the help of the Anisotropy of the Induced Current Density (AICD) method, developed by Herges and co-workers.[20] As shown in Fig. 1, the delocalization of the electrons within the seven-membered cyclic array produces the diatropic current responsible for the computed negative NICS value at the ring critical point.



Scheme 6 (4 + 3)-cycloaddition reaction of the parent oxyallyl cation **11**. Energy values are given in kcal mol^{-1} and bond distances in angstroms. All data have been computed at the B3LYP/def2-SVP level.

What is the effect of the metal fragment in the aromaticity of the analogous transition-metal catalyzed cycloaddition reaction? The computed NICS values at the (3,+1) ring critical point of the electron density of different transition-metal containing saddle points are highly negative as well (ranging from −16.3 to −17.6 ppm).[18] Therefore, it can be concluded that the metal-mediated (4 + 3)-cycloaddition reactions occurs through transition states that exhibit a higher *in-plane* aromatic character than the parent reaction involving an oxy-allyl cation. This is mainly due to the higher bond length equalization of the newly forming carbon–carbon bonds in these transition structures. If we assume that, in transition states, bonding equalization and synchronicity characterize aromatic structures,[21] it is not surprising that the observed higher bond equalization (compared to that in the parent **TSa**) is translated into a slightly higher aromaticity. Furthermore, synchronicity values close to the perfect synchronicity (S_y = 1.0) have been computed for reactions involving AuCl and AuPPh$_3$ metal fragments, thus indicating that metal-mediated

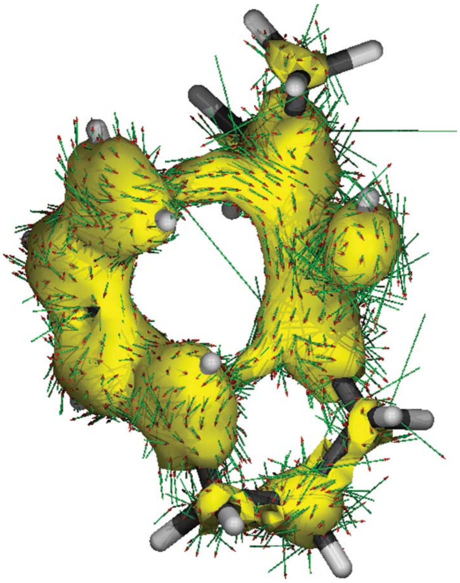


Fig. 1 AICD plot of **TSa**.

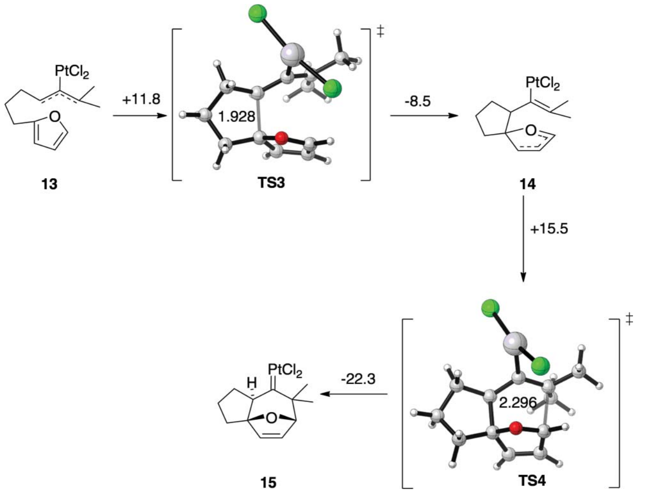
transformations can be even more synchronous than the corresponding parent reaction of the hydroxyallylic cation **11**. This behaviour is in sharp contrast to other metal assisted cycloadditions like [3 + 2] or [4 + 2] processes,[19c,g] which occur with lower values of synchronicity respect to the corresponding non-organometallic reactions.

Interestingly, one of the most striking differences between the non-organometallic process and the corresponding metal-mediated cycloaddition reaction is the strong bond polarization induced by the presence of the metal moiety. This is reflected in the computed significant positive charge (up to 0.24*e*) at the terminal allenyl-carbon atom which facilitates the addition of the double bond of the diene fragment leading to more compact (*i.e.* more synchronous) transition states. In contrast, the computed charge at the analogous carbon atom in the parent oxyallyl cation **11** was calculated to be +0.09*e* which translates into a more asynchronous saddle point.[18]

In addition, the metal fragment controls the characteristics of the LUMO of the initial allenediene reactants, which can be viewed as the π* molecular orbital of the allylic moiety. In fact, the second-order perturbation theory of the Natural Bond Orbital (NBO) method[22] clearly shows that this π* orbital is stabilized by two-electron delocalizations from the occupied d atomic orbital of the transition metal. As the LUMO is involved in the cycloaddition process (*vide infra*), the effect of the metal fragment in this transformation is in part due to these stabilizing interactions.

3.2. Concerted *vs.* stepwise reaction mechanisms

As described above, the intramolecular (4 + 3)-cycloaddition reaction involving the oxyallyl cation **11** (Scheme 6) as well as the analogous metal-mediated process (Scheme 2) occur concertedly through the *exo*-like transition states **TSa** and **TS1**, respectively. However, it was found that when furan acts as the diene moiety instead of 1,3-butadiene, the transformation proceeds stepwise through the formation of the σ-complex **14** in both cases (Scheme 7).[18] Both reaction steps are kinetically more difficult for the process involving $PtCl_2$ than for the parent oxyallyl cation in view of the higher computed activation barriers. Despite that, the presence of the metal moiety does not alter the topology of the reaction coordinate, which is mainly dominated by the diene fragment. This differential behaviour can be ascribed to the higher nucleophilic character of furyl-dienes compared to 1,3-butadiene which increases the net charge transfer towards the electrophilic allyl-moiety. This finding is in line with previous calculations reported by Harmata and Schreiner[23] and by Cramer and co-workers[24] who concluded that reactive and strongly electrophilic allylic cations and nucleophilic dienes tend to react *via* stepwise mechanisms, while less electrophilic cations and less nucleophilic dienes tend to react *via* concerted processes.



Scheme 7 Stepwise Pt(II)-catalysed (4 + 3)-cycloaddition reaction. Energy values are given in kcal mol^{-1} and bond distances in angstroms. All data have been computed at the B3LYP/def2-SVP level.

The potential energy surfaces of the intramolecular cycloaddition reaction of the parent oxyallyl-cations **11a** and **11b** (Chart 1) are depicted in Fig. 2. In the concerted pathway, interaction between both C3–C7 and C1–C10 pairs is required, through the corresponding molecular orbitals in which appropriate symmetries ensure a cyclic electronic delocalization associated with an aromatic transition structure. Differently, the first step of the stepwise mechanism involves the nucleophilic attack of C7 to C3, with an electronic displacement to generate an enol moiety (Chart 1).

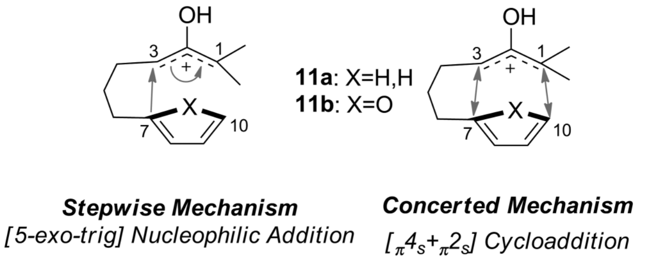


Chart 1

The possible reaction paths for **11a** (Fig. 2A) reveal a smooth surface in which only **TSa** can be found as a saddle point connecting **11a** and the corresponding (4 + 3)-cycloadduct *via* an *intramolecular* concerted mechanism. A similar inspection of the projected potential energy surface for the transformation involving

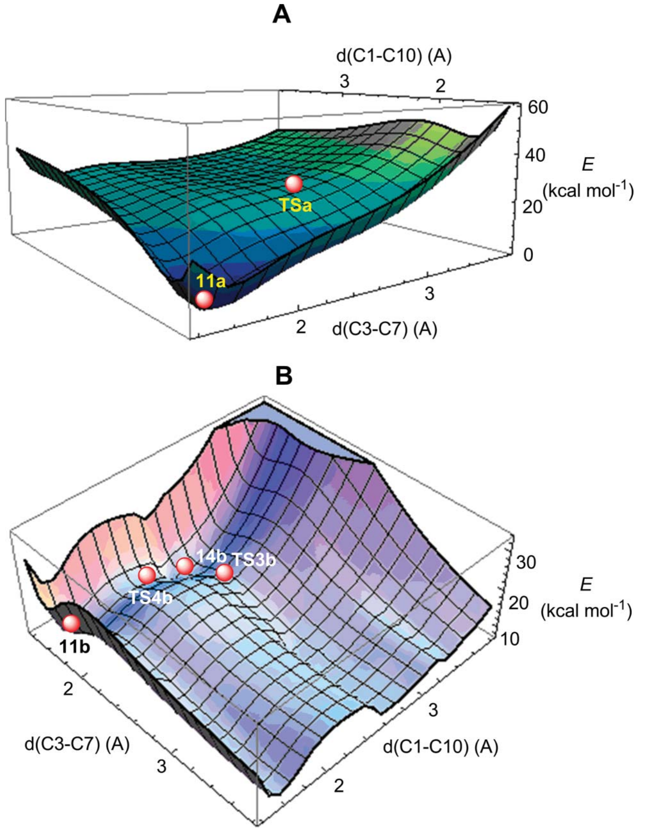


Fig. 2 Potential energy surfaces of the (4 + 3)-cycloaddition reactions of oxyallyl cations **11a** and **11b**.

the furan derivative **11b** (Fig. 2B) reveals a stepwise mechanism with intermediate **14b** connecting reactant and product *via* **TS3b** and **TS4b**.

The origins of this differential behaviour can be found in the different interaction of the involved molecular orbitals, *i.e.* HOMO–LUMO and (HOMO−1)–(LUMO+1) two-electron interactions. It was found that the stepwise mechanism is the preferred one along most of the potential energy surfaces associated with the initial stages of the processes involving **11a** and **11b**. This is due to the highly electrophilic character of the cationic allyl moiety of both reactants which hampers the cyclic electronic circulation required to complete the pericyclic mechanism. It is important to note that in the neighbourhood of **TSa** the concerted mechanism turns out to be the preferred one, in nice agreement with the computed shorter C3–C7 distance compared to the corresponding C1–C10 bond length.[18]

4. Summary and outlook

Herein, we have summarized the recent advances in the intramolecular (4 + 3)-cycloaddition reaction of allenedienes acting as allylic cations surrogates upon exposure to transition metal catalysts (Pt(II) and Au(I) salts). This process, which overcomes the main limitations of the analogous non-organometallic reaction involving oxy- and amino-allyl cations, has emerged as a powerful tool for the construction of not only complex seven-membered rings containing compounds but also different types of useful molecular skeletons by the proper selection of the catalyst. The transformation proceeds with high chemo- and stereoselectivity mainly because it occurs through an *exo*-like concerted transition state which exhibits a clear *in-plane* aromatic character. Despite that, stepwise reaction mechanisms are also possible when furan serves as diene in the cycloaddition instead of 1,3-butadiene. This is primarily ascribed to the higher nucleophilic character of furyldienes compared to 1,3-butadiene which increases the net charge transfer towards the electrophilic allyl-moiety.

One should expect major breakthroughs in the development of this useful reaction due to its high sensitivity to slight modifications of the steric and electronic properties of the metal moiety as well as the initial allenediene reactant. The future advances will be interesting in organic synthesis and also from a more fundamental point of view, as novel reaction mechanisms may evolve (*i.e.* from concerted to stepwise processes involving zwitterionic or even diradical intermediate species).

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Notes and references

1 (*a*) A. W. Fort, *J. Am. Chem. Soc.*, 1962, **84**, 2620; (*b*) A. W. Fort, *J. Am. Chem. Soc.*, 1962, **84**, 2625; A. W. Fort, *J. Am. Chem. Soc.*, 1962, **84**, 4979.
2 For reviews on (4 + 3) cycloaddition chemistry, see: (*a*) J. H. Rigby and F. C. Pigge, *Org. React*, 1997, **51**, 351; (*b*) M. Harmata, *Adv. Cycloaddit.*, 1997, **4**, 41; (*c*) M. Harmata, *Recent Res. Dev. Org. Chem.*, 1997, **1**, 523; (*d*) M. Harmata, *Tetrahedron*, 1997, **53**, 6235; (*e*) J. K. Cha and J. Oh, *Curr. Org. Chem.*, 1998, **2**, 217; (*f*) M. Harmata, *Acc. Chem. Res.*, 2001, **34**, 595.
3 (*a*) M. Harmata, *Chem. Commun.*, 2010, **46**, 8886; (*b*) M. Harmata, *Chem. Commun.*, 2010, **46**, 8904.
4 Catalytic examples of direct [4C + 3C] cycloadditions are very rare and essentially limited to the use of furan as diene, see: (*a*) M. Harmata, S. K. Ghosh, X. Hong, S. Wacharasindhu and P. Kirchhoefer, *J. Am. Chem. Soc.*, 2003, **125**, 2058; (*b*) M. Harmata, J. A. Brackley III and C. L. Barnes, *Tetrahedron Lett.*, 2006, **47**, 8151.
5 (*a*) F. López and J. L. Mascareñas, *Chem.–Eur. J.*, 2011, **17**, 418; (*b*) C. Aubert, L. Fensterbank, P. Garcia, M. Malacria and A. Simonneau, *Chem. Rev.*, 2011, **111**, 1954; (*c*) F. López and J. L. Mascareñas, *Beilstein J. Org. Chem.*, 2011, **7**, 1075.
6 B. Trillo, F. López, M. Gulías, L. Castedo and J. L. Mascareñas, *Angew. Chem., Int. Ed.*, 2008, **47**, 951.
7 B. Trillo, F. López, S. Montserrat, G. Ujaque, L. Castedo, A. Lledós and J. L. Mascareñas, *Chem.–Eur. J.*, 2009, **15**, 3336.
8 P. Mauleón, R. M. Zeldin, A. Z. González and F. D. Toste, *J. Am. Chem. Soc.*, 2009, **131**, 6348.
9 B. W. Gung, D. T. Craft, L. N. Bailey and K. Kirschbaum, *Chem.–Eur. J.*, 2010, **16**, 639.
10 (*a*) I. Alonso, B. Trillo, F. López, S. Montserrat, G. Ujaque, L. Castedo, A. Lledós and J. L. Mascareñas, *J. Am. Chem. Soc.*, 2009, **131**, 13020; (*b*) S. Montserrat, I. Alonso, F. López, J. L. Mascareñas, A. Lledós and G. Ujaque, *Dalton Trans.*, 2011, **40**, 1195.
11 D. Benitez, E. Tkatchouk, A. Z. González, W. A. Goddard and F. D. Toste, *Org. Lett.*, 2009, **11**, 4798.
12 M. R. Luzung, P. Mauleón and F. D. Toste, *J. Am. Chem. Soc.*, 2007, **129**, 12402.
13 M. Alcarazo, T. Stork, A. Anoop, W. Thiel and A. Fürstner, *Angew. Chem., Int. Ed.*, 2010, **49**, 2542.
14 (*a*) B. W. Gung and D. T. Craft, *Tetrahedron Lett.*, 2009, **50**, 2685; (*b*) B. W. Gung, D. T. Craft, L. N. Bailey and K. Kirschbaum, *Chem.–Eur. J.*, 2010, **16**, 639.

15 S. Aoki, M. Watanabe, M. Sanagawa, A. Setiawan, N. Kotoku and M. Kobayashi, *J. Am. Chem. Soc.*, 2006, **128**, 3148.

16 Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta and P. v. R. Schleyer, *Chem. Rev.*, 2005, **105**, 3842.

17 Given the unsymmetrical character of these cyclic systems, we needed to define the inner points of this system unambiguously. The (3,+1) ring critical point of the electron density, as defined by Bader (R. F. W. Bader, *Atoms in Molecules-A Quantum Theory*; Clarendon Press: Oxford, 1990; pp 12–52) is an unambiguous choice for the calculation of the NICSs, since only at this point is the electron density a minimum with respect to motion on the ring's plane and maximum with respect to motion perpendicular to the plane defined by the ring. The calculations were carried out at the GIAO-B3LYP/def2-SVP//B3LYP/def2-SVP level.

18 I. Fernández, F. P. Cossío, A. de Cózar, A. Lledós and J. L. Mascareñas, *Chem.–Eur. J.*, 2010, **16**, 12147.

19 (*a*) I. Morao, B. Lecea and F. P. Cossío, *J. Org. Chem.*, 1997, **62**, 7033; (*b*) F. P. Cossío, I. Morao, H. Jiao and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1999, **121**, 6737; (*c*) I. Fernández, M. A. Sierra and F. P. Cossío, *J. Org. Chem.*, 2006, **71**, 6178; (*d*) I. Fernández, M. A. Sierra and F. P. Cossío, *J. Org. Chem.*, 2007, **72**, 1488; (*e*) I. Fernández, F. P. Cossío and M. A. Sierra, *Organometallics*, 2007, **26**, 3010; (*f*) G. Frenking, F. P. Cossío, M. A. Sierra and I. Fernández, *Eur. J. Org. Chem.*, 2007, 5410; (*g*) I. Fernández, M. A. Sierra and F. P. F. P. Cossío, *J. Org. Chem.*, 2008, **73**, 2083; (*h*) I. Fernández, F. P. Cossío and F. M. Bickelhaupt, *Chem.–Eur. J.*, 2009, **15**, 13022; (*i*) I. Fernández and F. P. Cossío, *Curr. Org. Chem.*, 2010, **14**, 1578; (*j*) I. Fernández, F. P. Cossío and F. M. Bickelhaupt, *J. Org. Chem.*, 2011, **76**, 2310; (*k*) D. M. Andrada, A. M. Granados, M. Solà and I. Fernández, *Organometallics*, 2011, **30**, 466.

20 (*a*) R. Herges and D. Geuenich, *J. Phys. Chem. A*, 2001, **105**, 3214; (*b*) D. Geuenich, K. Hess, F. Köhler and R. Herges, *Chem. Rev.*, 2005, **105**, 3758.

21 (*a*) P. v. R. Schleyer, H. Jiao, M. N. Glukhoutsev, J. Chandrasekhar and E. Kraka, *J. Am. Chem. Soc.*, 1994, **116**, 10129; (*b*) P. v. R. Schleyer and H. Jiao, *Pure Appl. Chem.*, 1996, **68**, 209 and references therein.

22 (*a*) J. P. Foster and F. Weinhold, *J. Am. Chem. Soc.*, 1980, **102**, 7211; (*b*) A. E. Reed and F. Weinhold, *J. Chem. Phys.*, 1985, **83**, 1736; (*c*) A. E. Reed, R. B. Weinstock and F. Weinhold, *J. Chem. Phys.*, 1985, **83**, 735; (*d*) A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899.

23 M. Harmata and P. R. Schreiner, *Org. Lett.*, 2001, **3**, 3663.

24 (*a*) C. J. Cramer and S. E. Barrows, *J. Phys. Org. Chem.*, 2000, **13**, 176; (*b*) C. J. Cramer and S. E. Barrows, *J. Org. Chem.*, 1998, **63**, 5523.