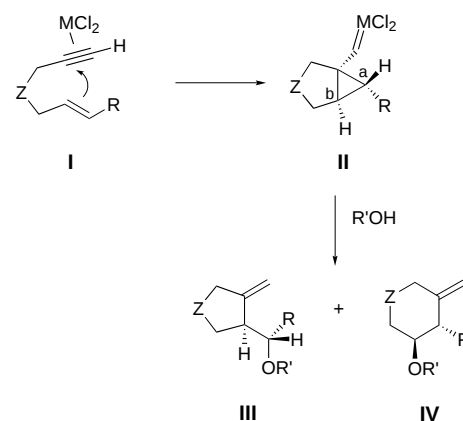


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- [10] Crystal data for [Cu(en)₃][Cu(CN)₃]: Blue parallelepiped crystals of dimensions $0.50 \times 0.38 \times 0.28 \text{ mm}^3$; Monoclinic, space group $P2_1/n$, $a = 7.6690(9) \text{ \AA}$, $b = 17.2770(19) \text{ \AA}$, $c = 12.4609(13) \text{ \AA}$, $\beta = 95.038(9)^\circ$, $V = 1644.7(3) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calcd}} = 1.557 \text{ Mg m}^{-3}$, $2\theta_{\text{max}} = 55^\circ$, $\mu(\text{Mo K}\alpha) = 2.591 \text{ mm}^{-1}$, ω scans, $\lambda = 0.71073 \text{ \AA}$; the data were collected at 130(2) K on a Siemens P3 diffractometer; a total of 4171 reflections were measured, of which 3769 were independent ($R_{\text{int}} = 0.044$) and included in the refinement; $\text{mim./max. transmission} = 0.3574/0.5307$; solution by direct methods (SHELXS-97, Sheldrick, **1990**); refinement by full-matrix least squares based on F^2 (SHELXTL 6.10, XL, Sheldrick, **2000**); 217 parameters, $R1 = 0.0811$, $wR2 = 0.1109$ for all data; $R1 = 0.0463$ computed for 2532 observed data ($I > 2\sigma(I)$).^[9b]
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- [18] The flocculent white precipitate formed upon reaction of [Cu(dmppy)(en)] with CH₃CN and ethylenediamine was separated by centrifugation and dried under vacuum.
- [19] One of the reviewers has suggested that a amide-bound Cu^{III} could be involved in the mechanism of the C–C bond cleavage of acetonitrile. Although this appears to be plausible, we do not have any spectroscopic evidence of an intermediate containing trivalent copper at this time.

Pt^{II}-Catalyzed Intramolecular Reaction of Furans with Alkynes**

Belén Martín-Matute, Diego J. Cárdenas, and Antonio M. Echavarren*

The coordination of electrophilic PtCl₂ to the C≡C bond of an enyne (**I**, Scheme 1) promotes intramolecular reaction of the alkene to form a cyclopropyl Pt carbene intermediate **II**.^[1, 2] Subsequent attack of an alcohol or water at the cyclopropyl carbon atoms C_a and C_b of **II** leads to the formation of five- or six-membered carbo- or heterocyclic rings under catalytic conditions.^[1]



Scheme 1. Metal-induced reaction of enynes to yield five- or six-membered rings.

These cyclizations are also catalyzed by AuCl₃ and some Ru^{II} complexes.^[1] In this regard, the recent finding that the intramolecular reaction of furans with alkynes can be catalyzed by AuCl₃ to afford phenols is of considerable interest.^[3, 4] The reaction was proposed to proceed by a [4+2] cycloaddition of the furan to the alkyne followed by cleavage of the resulting oxabicyclic adduct.^[3] Although this mechanistic proposal is reasonable, the related intramolecular reaction of arenes with alkynes with catalysis by Pt^{II} or Ru^{III}^[5] was proposed to take place by electrophilic aromatic substitution with an (η^2 -alkyne)metal electrophile.

We have found that 5-furyl-1-alkynes are also cyclized by PtCl₂ as catalyst. Several intermediate products could be obtained by conducting the reaction in an aqueous solvent. A clearer picture of the mechanism was obtained by performing

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Supporting information for this article is available on the WWW under <http://www.angewandte.com> or from the author.

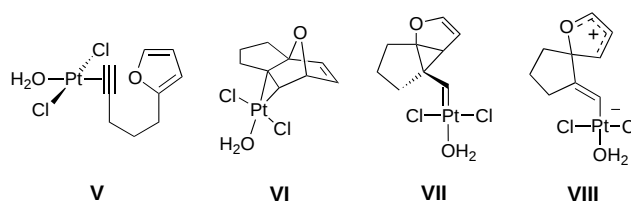
density functional calculations (DFT) on the intramolecular reaction of a furan with an alkyne coordinated to PtCl_2 .

The cyclization of 2-furylmethyl propargyl ether (**1**) was carried out in the presence of PtCl_2 (5 mol %) as catalyst in refluxing acetone to give phenols **2** (44 %) and **3** (16 %) (Scheme 2).^[6] Malonate **4** gave a mixture of phenols **5** (54 %) and **6** (16 %). Similar results were obtained with $[\text{PtCl}_2(\text{MeCN})_2]$ as catalyst. The cyclization of ether **1** with AuCl_3 (3 mol %) as catalyst in MeCN at room temperature also afforded a mixture of **2** and **3**, although the yields were lower (30 and 1.5 %, respectively). Cyclization of **7** led selectively to phenol **8** (75 %).^[7]

When these reactions were performed in the presence of water, in addition to the phenols, 2,5-dihydrofurans were also obtained in variable yields. Thus, **7** reacted in 10 % aqueous acetone under reflux with PtCl_2 (5 mol %) to furnish a mixture of phenol **8** (38 %), and ketoaldehydes **9** (4 %) and **10** (11 %). On the other hand, ether **11** with a terminal phenyl group gave ketoaldehyde **12** (24 %).

The formation of dicarbonyl compounds **9**, **10**, and **12** cannot easily be accounted for by a [4+2] cycloaddition pathway. To determine the nature of the reaction profile for the intramolecular reaction of alkynes and furans, we therefore performed DFT calculations on a model compound. Several pathways can be envisaged in principle, starting with coordination of the alkyne to the metal center (**V**), which was assumed to be also coordinated by a water molecule. First, a Diels–Alder reaction between the furan and the coordinated alkyne could give intermediate **VI**.^[3] Alternatively, formation of a cyclopropyl Pt carbene^[1] **VII** by reaction of the alkyne with the C2–C3 double bond of furan could occur. A third

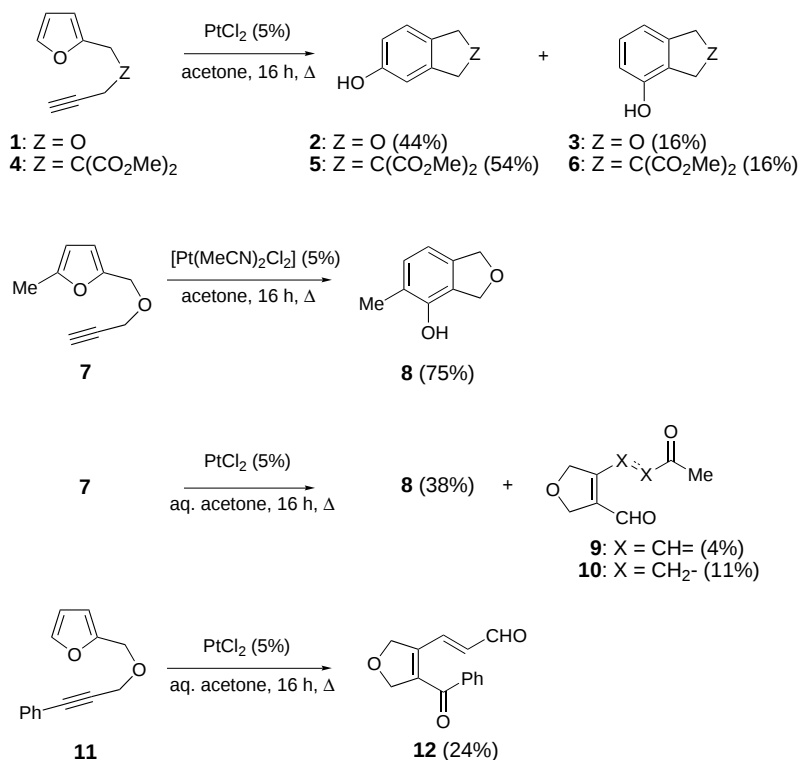
plausible mechanism involves a Friedel–Crafts-type reaction of the electron-deficient alkyne at C2 of the furan via **VIII**.^[5]



We searched for different reaction products that could be formed from **V**.^[8, 9] The Diels–Alder *endo* adduct **VI** (Figure 1) was located as a minimum of higher energy than **V** (+8.5 kcal mol^{−1}). The corresponding transition state **TS_{V,VI}** shows relatively short C–C distances for the bonds that are being formed, especially for that involving the alkyne terminal C atom (2.025 Å) and lies 30.2 kcal mol^{−1} above **V**. The carbon atoms of the coordinated alkene in **VI** are substantially pyramidalized, and the structure resembles a platinacyclopropane. The Cl–Pt–Cl angle diminishes from **V** to **VI** (171.6 to 161.9°) because of the steric hindrance imposed by the side chain. Alternatively, the internal C atom of the alkyne might react with the nucleophilic C2–C3 bond of the furan to give the cyclopropylcarbene **VII**. This complex shows a very short C(sp²)–Pt distance (1.890 Å), in accord with the carbene character. The formation of **VII** is exothermic (−3.4 kcal mol^{−1}), and the activation energy to reach transition state **TS_{V,VII}** is much lower (9.4 kcal mol^{−1}) than that of the Diels–Alder reaction. The attack of the furan takes place on the opposite side to the metal atom through an early

asymmetric transition state with very different C–C distances (2.293 and 2.528 Å for Pt–C2' and Pt–C3', respectively). This would be the preferred pathway for both thermodynamic and kinetic reasons. The formation of intermediate **VIII** was also considered, but the only minimum-energy structure that could be located when trying to obtain a minimized Friedel–Crafts complex was again **VII**. Apparently, the delocalization of the positive charge in **VIII** is not enough to compensate for the stability of the Pt cyclopropylcarbene.

These findings led to a mechanistic proposal summarized in Scheme 3. The initially formed complex **IX** would evolve exothermically to form key intermediate **X**. Cleavage of the cyclopropane and the dihydrofuran rings would form **XI**, which could be trapped by water to form dicarbonyl compounds such as **9**, **10**, and **12**.^[10] An intramolecular [2+2] cycloaddition of the platinum carbene with the carbonyl group could then give **XII**, which would undergo reductive elimination to give epoxide **XIII**.^[11] This last intermediate, which explains the formation of the isolated phenols, has also been proposed in the Au^{III}-catalyzed synthesis of phenols.^[3]



Scheme 2. Intramolecular reaction of furans with alkynes in the absence and in the presence of water.

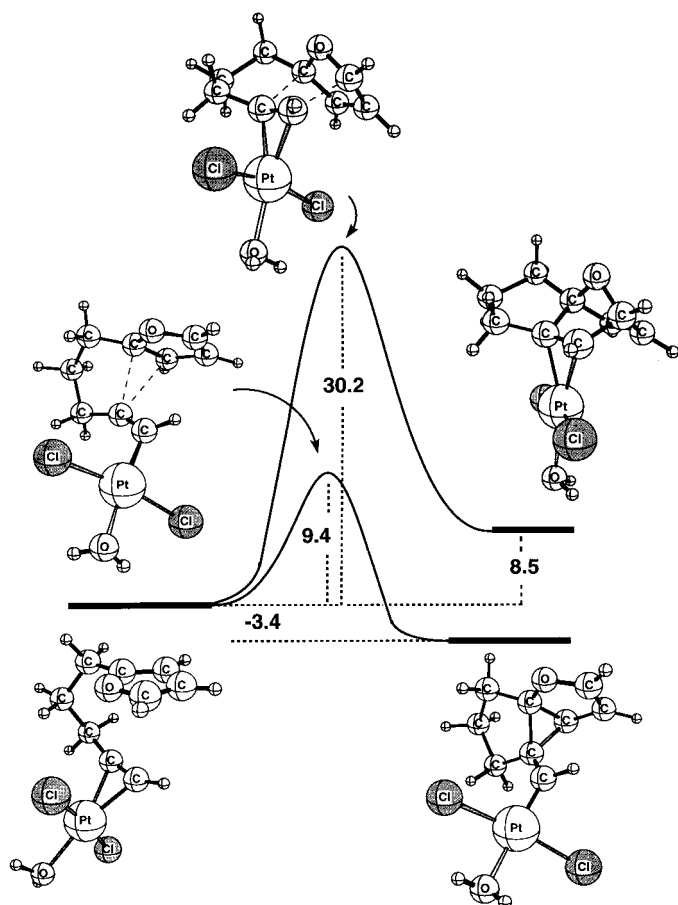
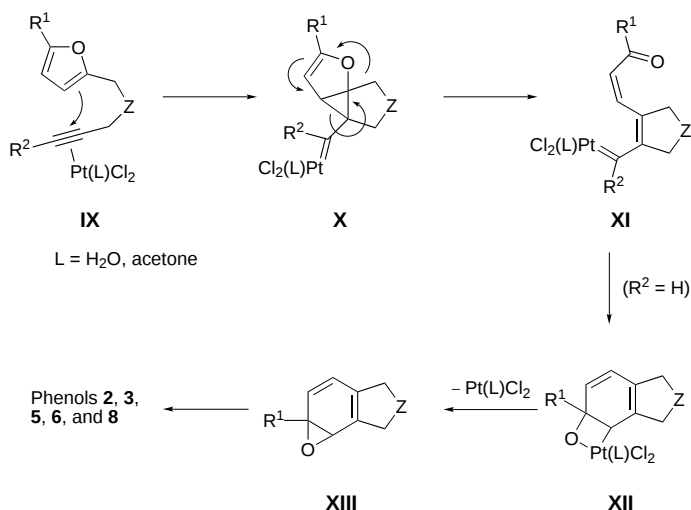
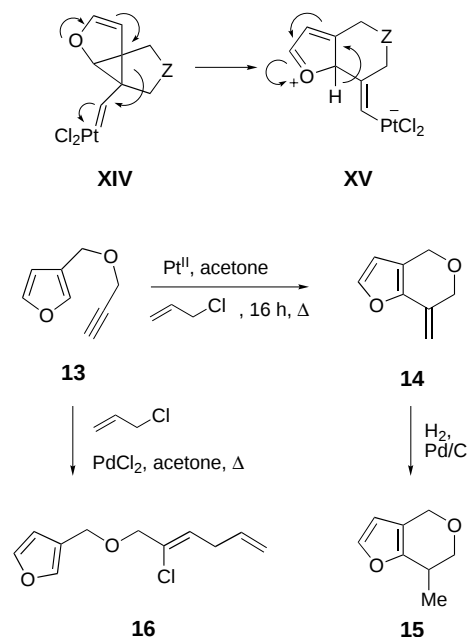


Figure 1. Reaction coordinate for two alternative reaction pathways of Pt^{II} complex **V** to give **VI** or **VII**. Energies in kcal mol^{-1} at the B3LYP/6-31G(d) level including ZPE correction.



Scheme 3. Mechanistic proposal.

Attaching the alkyne-containing chain at C3 of the furan was therefore expected to give **XIV**, which might evolve to form **XV** by cleavage of the cyclopropyl ring, followed by rearomatization (Scheme 4). Alternatively, **XV** could be formed by a direct electrophilic aromatic substitution pathway. In fact, treatment of 3-furymethyl propargyl ether (**13**)



Scheme 4. Reactions with a 2-substituted furan.

with PtCl_2 (5 mol %) led to **14** as the only new product, although the yield of isolated product was low because of its ready polymerization. For this reason, the crude product was immediately hydrogenated to give **15**. Curiously, the best result (34 % overall yield) was realized in the presence of allyl chloride, although the role of this additive is not yet known.^[12] In contrast, the use of $[\text{PdCl}_2(\text{MeCN})_2]$ (5 mol %) as catalyst (Et_2O , reflux) led only to the chloroallylation of the terminal alkyne to give **16**.^[13]

In summary, the intramolecular reaction of furans with alkynes catalyzed by PtCl_2 is mechanistically related to that of enynes in polar solvents^[11] and is initiated by the nucleophilic attack of the furan on an $(\eta^2\text{-alkyne})\text{platinum(II)}$ complex to form a cyclopropyl platinum carbene. This work suggests that similar transformations could be carried out with other electron-rich heterocycles and alkynes.

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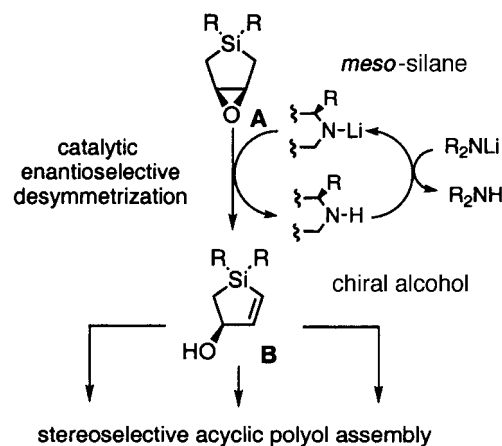
- [7] The reaction of **7** with AuCl_3 as catalyst afforded exclusively phenol **8** (69 %).^[3] In the platinum(II)-catalyzed reaction, traces (ca. 1 %) of a phenol tentatively assigned as 1,3-dihydro-6-methyl-5-isobenzofuranol were also obtained.
- [8] a) The calculations were performed with Gaussian98.^[8b] The geometries of all complexes were optimized at the DFT level of theory with the generalized gradient approximation and the B3LYP hybrid functional.^[8c, d] The standard 6-31G(d) basis set was used for C, H, O and Cl, and the default LANL2DZ pseudorelativistic potential and basis set were used for Pt. Harmonic frequencies were calculated at B3LYP level to characterize the stationary points and to determine the zero-point energies (ZPE). The starting approximate geometry for the transition states (TS) were located graphically; b) Gaussian98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1998.; c) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623–11627; d) W. Kohn, A. D. Becke, R. G. Parr, *J. Phys. Chem.* **1996**, *100*, 12974–12980.
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Catalytic Enantioselective Isomerization of Silacyclopentene Oxides: New Strategy for Stereocontrolled Assembly of Acyclic Polyols**

Dong Liu and Sergey A. Kozmin*

Creation of molecular chirality by desymmetrization of readily available prochiral precursors is a powerful synthetic strategy.^[1] This approach is particularly attractive when a substoichiometric amount of chiral catalyst is utilized to mediate such transformations with high efficiency and enantioselectivity.^[2] We have been engaged in the development of new catalytic desymmetrization approaches based on the use of cyclic silicon-containing templates. Herein, we disclose a highly enantioselective base-promoted rearrangement of silacyclopentene oxide, which resulted in the development of a novel strategy for the preparation of acyclic polyol-containing motifs. To our knowledge, enantioselective desymmetrization of cyclic silanes has not been documented prior to this work.^[3, 4]

Pioneered by Whitesell and Felman,^[5] base-mediated epoxide isomerization utilizing chiral lithium amides has become a valuable method for the preparation of allylic alcohols.^[6] With this as a precedent, we devised a strategy for desymmetrization of *meso*-silane **A** (Scheme 1). Enantioselective deprotonation, followed by β -elimination would result in the formation of enantiomerically enriched allylic alcohol **B**. Importantly, the use of a catalytic amount of chiral base in combination with an appropriate agent capable of regenerat-



Scheme 1. General strategy for the desymmetrization of *meso*-silane **A** to give enantiomerically enriched allylic alcohol **B**.

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