[3] J. March, *Advanced Organic Chemistry: Reactions Mechanisms and Structure*, 4th ed., Wiley, New York, **1992**, p. 723–724.

[4] F. B. Stocker, T. P. Staeva, C. M. Rienstra, D. Britton, *Inorg. Chem.* **1999**, *38*, 984–991.

[5] D. J. Chesnut, J. Zubieta, *Chem. Commun.* **1998**, 1707–1708.

[6] D. H. Gerlack, A. R. Kane, G. W. Parshall, J. P. Jesson, E. L. Muetterties, *J. Am. Chem. Soc.* **1971**, *93*, 3543-

[7] G. Favero, A. Morvillo, A. Turco, *Gazz. Chim. Ital.* **1979**, *109*, 27–28.

[8] D. S. Marlin, M. M. Olmstead, P. K. Mascharak, *Inorg. Chem.* **2001**, *40*, in press.

[9] a) Crystal data for [Cu(dmppy)(en)]: Blue plates of dimensions $0.35 \times 0.13 \times 0.06$ mm^3; monoclinic, space group $P2_1/n$, $a = 7.022(2)$, $b = 16.136(5)$, $c = 11.313(4)$ Å, $\beta = 93.11(2)^\circ$, $V = 1280.0(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.634$ Mg m^{-3}, $2\theta_{max} = 63^\circ$, $\mu(\mathrm{Mo}_{K\alpha}) = 1.713$ mm^{-1}, ω scans, $\lambda = 0.71073$ Å; the data were collected at 92(2) K on a Bruker SMART 1000 diffractometer; a total of 34867 reflections were measured, of which 9910 were independent ($R_{int} = 0.067$) and included in the refinement; mim./max. transmission = 0.5855/0.9042; solution by direct methods (SHELXS-97, Sheldrick, **1990**); refinement by full-matrix least-squares based on F^2 (SHELXTL 6.1, Sheldrick, **2001**); 175 parameters, $R1 = 0.0641$, $wR2 = 0.1254$ for all data; $R1 = 0.0460$ computed for 7282 observed data ($I > 2\sigma(I)$). b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-167732 [Cu(dmppy)(en)] and CCDC-167733 [Cu(en)$_3$][Cu(CN)$_3$]. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[10] Crystal data for [Cu(en)$_3$][Cu(CN)$_3$]: Blue parallelpiped crystals of dimensions $0.50 \times 0.38 \times 0.28$ mm^3; Monoclinic, space group $P2_1/n$, $a = 7.6690(9)$ Å, $b = 17.2770(19)$ Å, $c = 12.4609(13)$ Å, $\beta = 95.038(9)^\circ$, $V = 1644.7(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.557$ Mg m^{-3}, $2\theta_{max} = 55^\circ$, $\mu(\mathrm{Mo}_{K\alpha}) = 2.591$ mm^{-1}, ω scans, $\lambda = 0.71073$ Å; 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 ($R_{int} = 0.044$) and included in the refinement; 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]

[11] M. Wicholas, T. Wolford, *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 157–159.

[12] I. Bertini, P. Dapporto, D. Gatteschi, A. Scozzafava, *J. Chem. Soc. Dalton Trans.* **1979**, 1409–1414

[13] D. L. Cullen, E. C. Lingafelter, *Inorg. Chem.* **1970**, *9*, 1858-

[14] J. Pickardt, B. Staub, K. O. Schäfer, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1217–1224.

[15] P. Chaudhuri, K. Oder, K. Wieghardt, J. Weiss, J. Reedijk, W. Hinrichs, J. Wood, A. Ozarowski, H. Stratemaier, D. Reinen, *Inorg. Chem.* **1986**, *25*, 2951–2958.

[16] M. Wicholas, T. Wolford, *Inorg. Chem.* **1974**, *13*, 316–318.

[17] Solvent from the filtrate was removed under vacuum, and the residue was dissolved in H$_2$O and extracted with CH$_2$Cl$_2$. The organic layer was collected, dried, and solvent removed under vacuum to yield pure dmppyH$_2$.

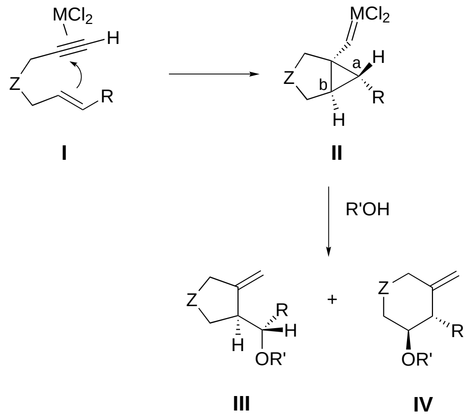
[18] The floculent white precipitate formed upon reaction of [Cu(dmppy)(en)] with CH$_3$CN and ethylenediamine was seperated by centrifugation and dried under vacuum.

[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 PtCl$_2$ 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 AuCl$_3$ and some Ru^{II} complexes.[1] In this regard, the recent finding that the intramolecular reaction of furans with alkynes can be catalyzed by AuCl$_3$ 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^{II}[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 PtCl$_2$ 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

---

[*] Prof. Dr. A. M. Echavarren, B. Martín-Matute, Dr. D. J. Cárdenas
Departamento de Química Orgánica
Universidad Autónoma de Madrid
Cantoblanco, 28049 Madrid (Spain)
Fax: (+349) 1-3973966
E-mail: anton.echavarren@uam.es

[**] This work was supported by the DGICYT (project PB97-0002) and the MCyT (predoctoral fellowship to B.M.-M.). We also acknowledge Johnson Matthey PLC for a generous loan of PtCl$_2$.

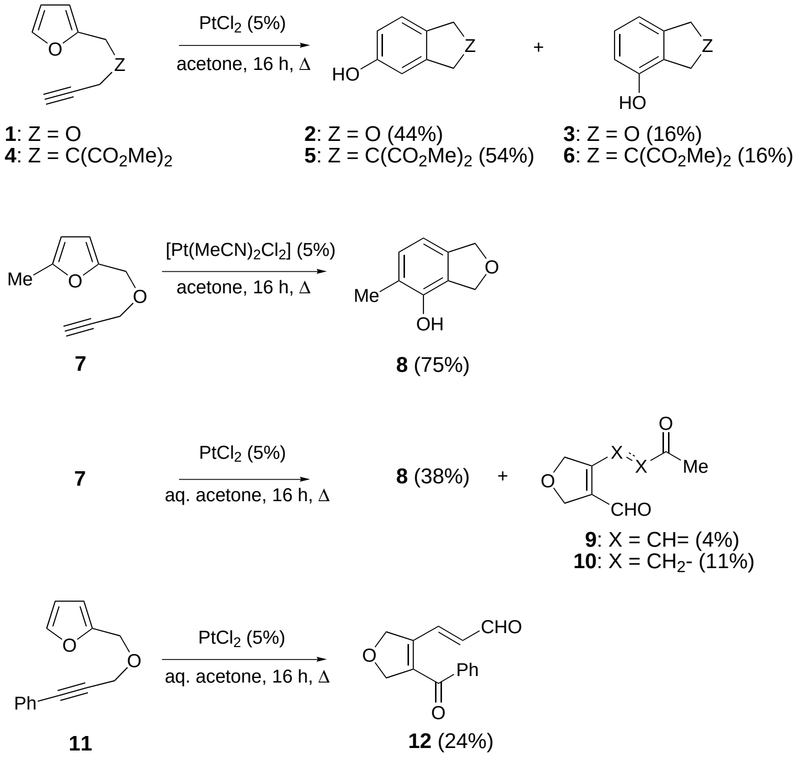
Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

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

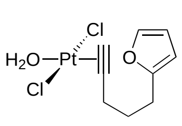
The cyclization of 2-furylmethyl propargyl ether (**1**) was carried out in the presence of $PtCl_2$ (5 mol%) as catalyst in refluxing acetone to give phenols **2** (44%) and **3** (16%) (Scheme 2).[6] Malonate **4** gave a mixture of phenols **5** (54%) and **6** (16%). Similar results were obtained with $[PtCl_2(MeCN)_2]$ 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%).

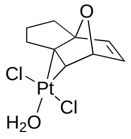
The formation of dicarbonyl compounds **9**, **10**, and **12** cannot easily be accounted for by a [4+2] cycloaddition pathway. To determine the nature of the reaction profile for the intramolecular reaction of alkynes and furans, we therefore performed DFT calculations on a model compound. Several 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]



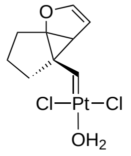
Scheme 2. Intramolecular reaction of furans with alkynes in the absence and in the presence of water.



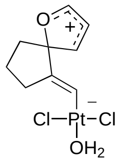
V



VI



VII



VIII

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 $\mathbf{TS_{V\text{-}VI}}$ 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°) bacause 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(sp^2)–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 $\mathbf{TS_{V\text{-}VII}}$ 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]

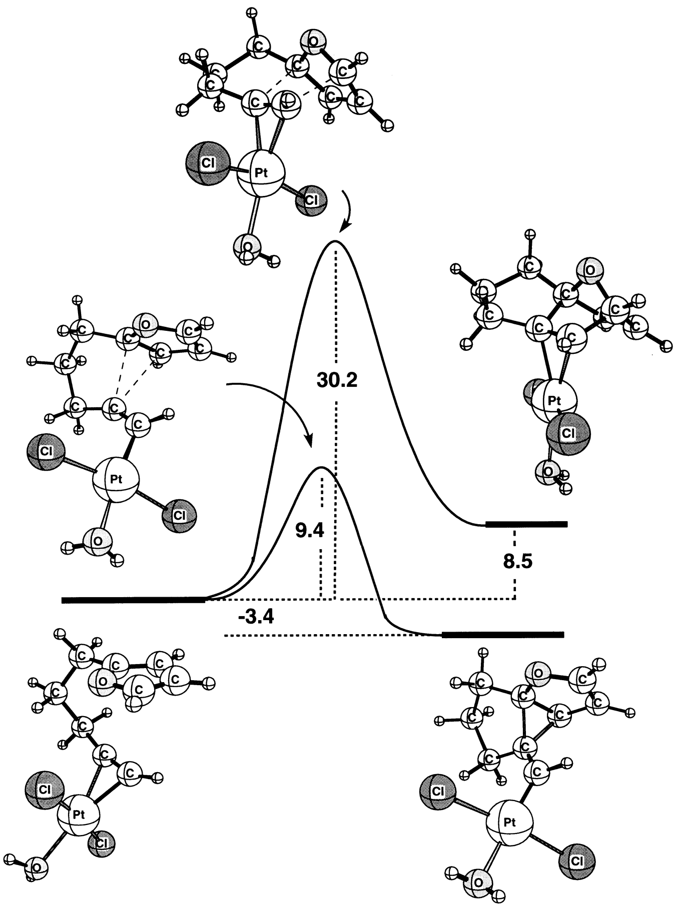
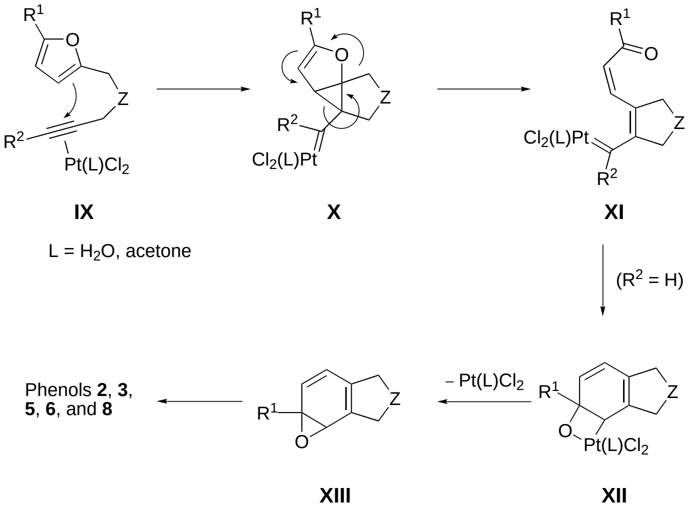
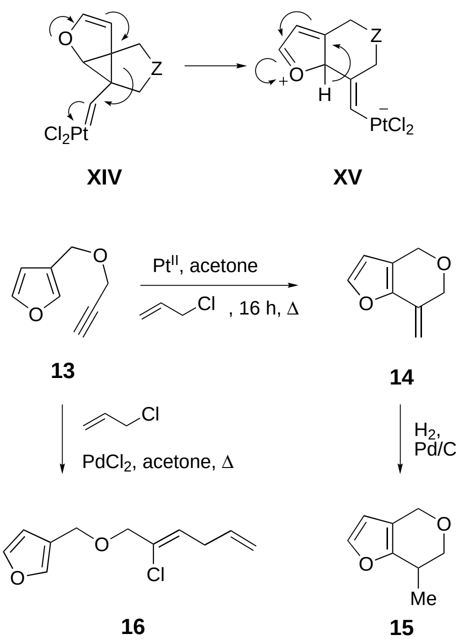


Figure 1. Reaction coordinate for two alternative reaction pathways of Pt^{II} complex **V** to give **VI** or **VII**. Energies in kcal mol^{-1} at the B3LYP/6-31G(d) level including ZPE correction.



Scheme 3. Mechanistic proposal.



Scheme 4. Reactions with a 2-substituted furan.

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-furylmethyl propargyl ether (**13**) 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 $[PdCl_2(MeCN)_2]$ (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[1] and is initiated by the nucleophilic attack of the furan on an (η^2-alkyne)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.

Received: August 2, 2001 [Z17658]

---

[1] a) M. Méndez, M. P. Muñoz, A. M. Echavarren, *J. Am. Chem. Soc.* **2000**, *122*, 11549–11550; b) M. Méndez, M. P. Muñoz, C. Nevado, D. J. Cárdenas, A. M. Echavarren, *J. Am. Chem. Soc.* **2001**, *123*, 10511–10520.

[2] a) B. M. Trost, M. J. Krische, *Synlett* **1998**, 1–16; b) N. Chatani, K. Kataoka, S. Murai, N. Furokawa, Y. Seki, *J. Am. Chem. Soc.* **1998**, *120*, 9104–9105; c) A. Fürstner, H. Szillat, F. Stelzer, *J. Am. Chem. Soc.* **2000**, *122*, 6785–6786; d) S. Oi, I. Tsukamoto, S. Miyano, Y. Inoue, *Organometallics* **2001**, *20*, in press.

[3] A. S. K. Hashmi, T. M. Frost, J. W. Bats, *J. Am. Chem. Soc.* **2000**, *122*, 11553–11554.

[4] For a highlight on the catalytic applications of gold, see G. Dyker, *Angew. Chem.* **2000**, *112*, 4407–4409; *Angew. Chem. Int. Ed.* **2000**, *39*, 4237–4239.

[5] N. Chatani, H. Inoue, T. Ikeda, S. Murai, *J. Org. Chem.* **2000**, *65*, 4913–4918.

[6] See the Supporting Information for experimental details and characterization data.

1433-7851/01/4024-4756 $ 17.50+.50/0

[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 Gaussian 98.[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) Gaussian 98 (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**, *1000*, 12974–12980.

[9] Bond lengths, bond angles, and atomic coordinates for the structures of Figure 1 are given in the Supporting Information.

[10] a) A mechanistic hypothesis for the formation of dihydrofurans from **XI** is outlined in the Supporting Information; b) we have previously observed the formation of an aldehyde from a related platinum carbene intermediate;[1b] c) for the related oxidation of a nickel carbene intermediate, see: S. K. Chowdhury, K. K. D. Amarasinghe, M. J. Heeg, J. Montgomery, *J. Am. Chem. Soc.* **2000**, *122*, 6775–6776.

[11] Rhodium carbenes, generated in situ from $[Rh_2(OAc)_4]$ and diazo compounds, react with aldehydes to form epoxides. See, for example, a) V. K. Aggarwal, H. Abdel-Rahman, R. V. H. Jones, H. Y. Lee, B. D. Reid, *J. Am. Chem. Soc.* **1994**, *116*, 5973–5974; b) M. Hamaguchi, H. Matsubara, T. Nagai, *Tetrahedron Lett.* **2000**, *41*, 1457–1460.

[12] Trapping of an intermediate alkenylmetal intermediate with allyl chloride: C. Fernández-Rivas, M. Méndez, A. M. Echavarren, *J. Am. Chem. Soc.* **2000**, *122*, 1221–1222.

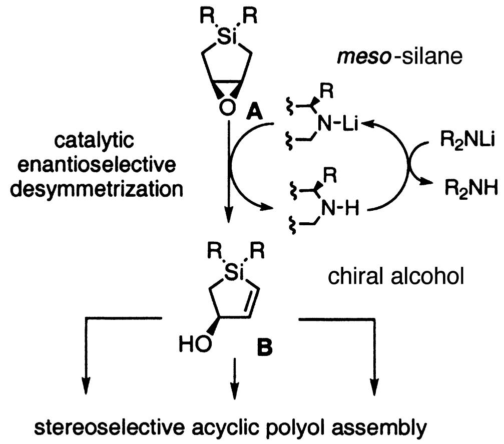
[13] a) K. Kaneda, T. Uchiyama, Y. Fujiwara, T. Imanaka, S. Teranishi, *J. Org. Chem.* **1979**, *44*, 55–63; b) J.-E. Bäckvall, Y. I. M. Nilsson, R. G. P. Gatti, *Organometallics* **1995**, *14*, 4242–4246, and references therein.

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 enatiomerically enriched allylic alcohol **B**.

---

[*] Prof. Dr. S. A. Kozmin, D. Liu
Department of Chemistry
University of Chicago
5735 South Ellis Avenue
Chicago, IL 60637 (USA)
Fax: (+1) 773-702-0805
E-mail: skozmin@uchicago.edu

[**] Initial funding of this work was provided by the University of Chicago. We are grateful to the donors of the Petroleum Research Fund for further financial support.

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