UV-induced immobilization of tethered zirconocenes on H-terminated silicon surfaces†

Heidrun Gruber-Woelfler,[a] Sandrine Rivillon Amy,[b] Yves J. Chabal,[b] Georg Schitter,[a] Eleonora Polo,[c] Markus Ringwald[d] and Johannes G. Khinast*[a]

Received (in Cambridge, UK) 19th November 2007, Accepted 24th January 2008
First published as an Advance Article on the web 15th February 2008
DOI: 10.1039/b717817d

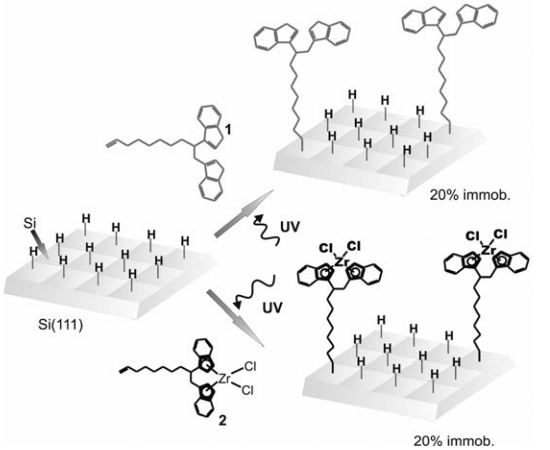
A tethered ethylenebis(indenyl) zirconocene was covalently immobilized on H-terminated Si(111) surfaces using UV-mediated alkene hydrosilylation, thus making possible the development of structured catalytic surfaces with highly controlled properties.

Functionalization of a single-crystal silicon surface is an area of intense research due to the potential use of hybrid organo–silicon as the basis for integrating various functionalities, such as molecular recognition devices,[1] organometallic complexes[2,3] and biomolecules, including proteins, DNA and carbohydrates.[4,5] Due to their wide use in microelectronic applications, single-crystal silicon wafers of high purity are commercially available and relatively inexpensive.[6] Taking advantage of the strong Si–C bond, the covalent immobilization of organometallic complexes onto crystalline silicon is a powerful approach to preparing catalytically active materials, which can be repeatedly recycled and do not show leaching. Prevention of metal leaching is especially important, *e.g.*, in pharmaceutical syntheses.[7]

In this communication we report the covalent attachment of a tethered chiral metallocene catalyst onto atomically flat H-terminated silicon(111) [H/Si(111)] surfaces using UV-mediated hydrosilylation. In addition to being a clean and straightforward approach, this method lends itself to the submicron structuring of catalytic surfaces *via* photopatterning and photolithography. Among the different methods developed to heterogenize metallocene catalysts,[8–14] immobilization using covalent tethering techniques is currently the most favored approach to designing stable heterogeneous asymmetric catalysts.[15] We recently reported the covalent immobilization of a tethered ethylenebis(indenyl) (= EBI) ligand on H-terminated Si(111) surfaces applying UV-mediated alkene hydrosilylation and verified that the hydrosilylation process follows an exciton electron-hole mechanism.[16] Hydride-terminated surfaces in general offer many advantages, including their excellent chemical homogeneity (>99% H-termination).[6] Furthermore, these surfaces are relatively stable in air for short periods of time. In contrast, the Si–X (X = Br, I) surfaces are much more reactive with respect to hydrolysis and Si–OH formation and can generally only be handled under an inert atmosphere.[6] The formation of silicon–carbon bonds can be performed by 'wet chemical' and ultrahigh vacuum (UHV) approaches. The wet chemical methods for Si–H terminated surfaces include (i) hydrosilylation involving a radical initiator,[17,18] (ii) thermally induced hydrosilylation,[19,20] (iii) photochemical hydrosilylation with UV light[21–23] and white light,[24,25] (iv) reactions of alkyl/aryl carbanions, and (v) electrochemical grafting, including electrochemical diazonium reductions,[26–29] reductive electrolysis of alkyl iodide, alkyl bromide, and benzyl bromide species[30] and others.[31] A thorough review of the literature has been given by Buriak.[6]

In this study we focus on the immobilization of a functional zirconocene complex (*i.e.*, 10-η^5-(1-indenylidene)-9-η^5-(1-indenylidene)-1-decene zirconium dichloride (**2**)) on an atomically flat H/Si(111) surface (Scheme 1), thus combining the mechanical, structural and electrical properties of silicon surfaces with the effectiveness of Group 4 metallocenes, which are known to be highly active and selective catalysts for reactions such as enantioselective hydrogenation,[32–34] hydrosilylation[35–37] and polymerization.[38,39]

While previous publications reported the UV-mediated hydrosilylation of alkenes, alkynes,[6] aldehydes,[23] and



Scheme 1 Immobilization of the tethered ligand **1** and the zirconocene **2**.

---

[a] Institute for Process Engineering, Graz University of Technology, Inffeldgasse 21A/II, A-8010 Graz, Austria. E-mail: khinast@tugraz.at
[b] Department of Chemistry and Chemical Biology, Rutgers University, 136 Frelinghuysen Road, NJ 08854 Piscataway, USA. E-mail: yves@agere.rutgers.edu
[c] C.N.R.-ISOF Sez. Ferrara, c/o Dip. di Chimica, Via L.Borsari 46, 44100 Ferrara, Italy. E-mail: tr3@unife.it
[d] MCAT GmbH, Hermann-von-Vicari-Str. 23, D-78464 Konstanz, Germany. E-mail: ringwald@mcat.de

† Electronic supplementary information (ESI) available: Experimental conditions and characterization of the new compounds. See DOI: 10.1039/b717817d

cyclodextrins,[1] as well as the dehydrogenative silane coupling on silicon *via* Cp_2ZrCl_2 and Cp_2TiCl_2,[12] this is the first study of Group 4 metallocene immobilization on Si(111) surfaces *via* UV-irradiation. We used this approach for the immobilization of the zirconocene complexes, as it can be carried out at room temperature, thus avoiding thermal input that might be detrimental for the organometallic complex. Additionally, this immobilization method does not require catalysts. Therefore, side reactions as well as post-contamination of the surface can be avoided.

The synthesis of the functional ligand 3-[2-(1*H*-inden-3-yl)dec-9-enyl]-1*H*-indene (**1**) was carried out through a synthetic pathway as recently reported by Panarello *et al.*[40] The metalation was performed by reaction of either (i) the lithium salt of **1** with $ZrCl_4$ or (ii) the potassium salt of **1** with $ZrCl_4 \cdot 2THF$ to give **2**. The NMR spectrum is consistent with the presence of a mixture of *rac*/*meso* isomers. The separation by physical methods of the isomers is difficult due to the high solubility of **2** in most organic solvents. However, it was possible to isolate two fractions (complexes **2a** and **2b**) with a different ratio of *rac*/*meso* isomers—complex **2a** contains a 50 : 50 ratio of *rac*/*meso*, while complex **2b** includes a larger amount of the *rac* isomer (ESI†). Both complexes were used for immobilization on H/Si(111). Preliminary experiments indicate that the tethered EBI-based zirconocene is active for the polymerization of propylene.[41] The corresponding titanocene (pure and immobilized) was shown to be active for the hydrosilylation of imines.[41]

Fig. 1 shows evidence of the attachment of the functional ligand **1** onto an atomically flat H/Si(111) surface using two different methods: UV-mediated (Fig. 1a) and thermal (Fig. 1b) hydrosilylation. The negative feature at 2083 cm^{-1} indicates that ~20% (UV-hydrosilylation) and ~35% (thermal hydrosilylation) of the hydrogen from the initial H-terminated silicon surface are removed by these treatments.[42] According to Hara *et al.*[2] and Sieval *et al.*,[43] a maximum of 50–55% of the inherent Si–H groups can be functionalized with simple long terminal alkenes. In both spectra the specific modes of the indene molecules are present, such as =C–H stretch of the benzene ring at ~3000–3100 cm^{-1}, the C=C–H stretch of the indene ring between 1400 and 1700 cm^{-1}, in-plane CH bend between 900 and 1300 cm^{-1}, out-of-plane CH bend between 700 and 1000 cm^{-1}, and finally CH_2 stretch and bend at 2926, 2850 and 1280 cm^{-1}.[44,45] The results regarding the loss of Si–H suggest that both hydrosilylation methods lead to a different surface density for the attached ligand **1**: upon thermal hydrosilylation more ligand **1** is immobilized on the H/Si(111) surface. However, the coverage observed for ligand **1** after thermal hydrosilylation (~35%) appears to be the highest considering the van der Waals radius of the molecules: no more than one third of the surface can be covered by the ligand. Finally, intensity differences of the hydrocarbon modes in Fig. 1 may be associated with different orientations of the adsorbed molecules. Notably, the CH_2 stretch and bend modes are more intense after thermal hydrosilylation, while =CH stretch and bend modes from the benzene ring are more intense after UV hydrosilylation.

Fig. 2 compares the spectra of the tethered ligand **1** and of the zirconocene complexes **2a** and **2b** immobilized on H/Si(111) *via* the UV-mediated reaction. The negative Si–H stretch feature at 2083 cm^{-1} and the presence of absorbance features similar to the ones observed in Fig. 1 suggest that complexes **2a** and **2b** have reacted with the H/Si(111) surface. It can be estimated that ~80–85% of the hydrogen atoms remain on the surface, indicating that the UV-mediated hydrosilylation process is independent of the presence of the zirconium: nearly the same amounts of ligand (~20%) with (**2a** and **2b**) or without zirconium metal (*i.e.*, ligand **1**) are attached to the silicon surface, suggesting that $ZrCl_2$ does not influence the hydrosilylation reaction. However, the spectra of the immobilized compounds indicate a clear change in the overall features due to the presence of the zirconium atoms: the CH_2 stretch modes appear to be less intense and less resolved when the zirconium atoms are coordinated to the tethered ligand while the deformation modes of the indene group are stronger. Since the relative amounts of ligand attached on the Si(111) are similar, the difference observed between the spectra suggests that the presence of $ZrCl_2$

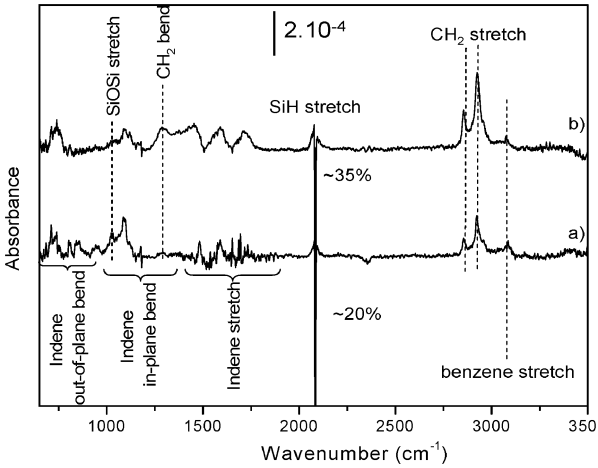


Fig. 1 Transmission IR spectra of 3-[2-(1*H*-inden-3-yl)dec-9-enyl]-1*H*-indene (**1**) attached to H/Si(111) using (a) UV and (b) thermal hydrosilylation. The reference spectrum is H/Si(111).

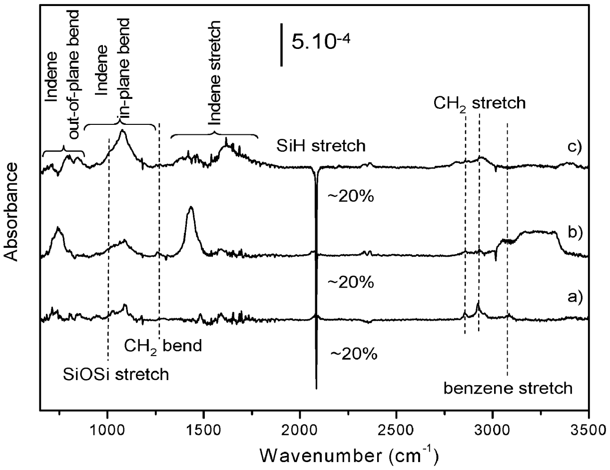


Fig. 2 Transmission IR spectra of (a) 3-[2-(1*H*-inden-3-yl)dec-9-enyl]-1*H*-indene (**1**), (b) zirconocene complex **2a** and (c) complex **2b** attached to H/Si(111). The reference spectrum is H/Si(111).

modifies the orientation of the chains, possibly due to interchain van der Waals interactions.

We also observed changes of the IR signatures depending on which complex is attached on the Si surface. This is because fractions **2a** and **2b** contain different ratios of the *rac*/*meso* isomers. In fact, the spectrum related to the hydrosilylation of **2a** (Fig. 2b) shows that two absorbance features at 1450 and 750 cm^{-1} are more intense than in the spectrum obtained for the immobilized ligand **1**. These modes have been previously attributed to the CH stretch and bend mode for four adjacent hydrogen atoms in the indene ring.[44] In contrast, in the case of *rac*-rich complex **2b**, the features at 1600 and 1100 cm^{-1} are more intense. These signals are characteristic of the CH stretch and bend mode of the indene ring and would be expected for *rac* isomers bonded to the H/Si(111) surface. This result suggests that mostly *rac* isomers are attached onto H/Si(111) (Fig. 2c). When the *rac*/*meso* isomer ratio is 50 : 50 (fraction **2a**, Fig. 2b), no preferential attachment of the isomers to the surface is observed: the IR spectrum exhibits a different signature, suggesting that *meso* isomers are also attached onto the H/Si(111) surface.

The presence of the zirconium atoms cannot be observed directly with IR spectroscopy, because the dipole moment of Zr vibrates below 400 cm^{-1}. However, analyses of the functionalized Si(111) samples by Rutherford backscattering (RBS) show a clear amount of zirconium for both complexes attached to the surface: $\sim 0.09 \times 10^{15}$ Zr cm^{-2}, *i.e.*, $\sim(16 \pm 2)\%$ of Zr for complex **2a** and $\sim 0.11 \times 10^{15}$ Zr cm^{-2}, *i.e.*, $\sim(20 \pm 2)\%$ for complex **2b**. These results are in agreement with the IR results, which indicate that 15–20% of **2a** and **2b** are attached.

In summary, we report the first controlled attachment of a metallocene onto H/Si(111) surfaces. The immobilization procedure involves a UV-mediated alkene hydrosilylation reaction, thus avoiding use of catalysts and harsh reaction conditions. This method may be suited to prepare highly controlled catalytic surfaces with a submicron structure.

We gratefully acknowledge the financial support of the Austrian Science Foundation (Project No. 19410). S. Rivillon Amy and Y. Chabal acknowledge the support of NSF (CHE-0415652) and stimulating discussions with L. Wielunski (Rutgers University).

Notes and references

1 C. Lagrost, G. Alcaraz, J.-F. Bergamini, B. Fabre and I. Serbanescu, *Chem. Commun.*, 2007, 1050.
2 K. Hara, S. Tayama, H. Kano, T. Masuda, S. Takakusagi, T. Kondo, K. Uosaki and M. Sawamura, *Chem. Commun.*, 2007, 4280.
3 A. Juang, O. A. Scherman, R. H. Grubbs and N. S. Lewis, *Langmuir*, 2001, **17**, 1321.
4 L. C. P. M. deSmet, G. A. Stork, G. H. F. Hurenkamp, Q. Y. Sun, H. Topal, P. J. E. Vronen, A. B. Sieval, A. Wright, G. M. Visser, H. Zuilhof and E. J. R. Sudholter, *J. Am. Chem. Soc.*, 2003, **125**, 13916.
5 T. Strother, W. Cai, X. Zhao, R. J. Hamers and L. M. Smith, *J. Am. Chem. Soc.*, 2000, **122**, 1205.
6 J. M. Buriak, *Chem. Rev.*, 2002, **102**, 1271.
7 D. Geoffroy and F. Hancock, *Specialty Chemicals Magazine*, 2002, **22**, 10.
8 H. G. Alt, *Dalton Trans.*, 2005, 3271.
9 F. Ciardelli, A. Altomare and M. Michelotti, *Catal. Today*, 1998, **41**, 149.
10 J. H. Z. dos Santos, H. T. Ban, T. Teranishi, T. Uozumi, T. Sano and K. Soga, *J. Mol. Catal. A: Chem.*, 2000, **158**, 541.
11 G. G. Hlatky, *Chem. Rev.*, 2000, **100**, 1347.
12 Y. H. Li and J. M. Buriak, *Inorg. Chem.*, 2006, **45**, 1096.
13 B. Peifer, W. Milius and H. G. Alt, *J. Organomet. Chem.*, 1998, **553**, 205.
14 G. Tang, G. X. Jin and L. Weng, *J. Organomet. Chem.*, 2004, **689**, 678.
15 P. McMorn and G. J. Hutchings, *Chem. Soc. Rev.*, 2002, **33**, 108.
16 A. Langner, A. Panarello, S. Rivillon, O. Vassylyev, J. G. Khinast and Y. J. Chabal, *J. Am. Chem. Soc.*, 2005, **127**, 12798.
17 C. Chatgilialoglu, *Acc. Chem. Res.*, 1992, **25**, 188.
18 M. R. Linford, P. Fenter, P. M. Eisenberger and C. E. D. Chidsey, *J. Am. Chem. Soc.*, 1995, **117**, 3145.
19 A. B. Sieval, A. L. Demirel, J. W. M. Nissink, M. R. Linford, J. H. van der Maas, W. H. de Jeu, H. Zuilhof and E. J. R. Sudholter, *Langmuir*, 1998, **14**, 1759.
20 R. Boukherroub, S. Morin, D. D. M. Wayner, F. Bensebaa, G. I. Sproule, J. M. Baribeau and D. J. Lockwood, *Chem. Mater.*, 2001, **13**, 2002.
21 R. L. Cicero, M. R. Linford and C. E. D. Chidsey, *Langmuir*, 2000, **16**, 5688.
22 R. Boukherroub, S. Morin, F. Bensebaa and D. D. M. Wayner, *Langmuir*, 1999, **15**, 3831.
23 F. Effenberger, G. Götz, B. Bidlingmaier and M. Wezstein, *Angew. Chem., Int. Ed.*, 1998, **37**, 2462.
24 M. P. Stewart and J. M. Buriak, *Angew. Chem., Int. Ed.*, 1998, **37**, 3257.
25 M. P. Stewart and J. M. Buriak, *J. Am. Chem. Soc.*, 2001, **123**, 7821.
26 P. Allongue, C. Henry de Villeneuve and J. Pinson, *Electrochim. Acta*, 2000, **45**, 3241.
27 B. Chen, A. K. Flatt, H. Jian, J. L. Hudson and J. M. Tour, *Chem. Mater.*, 2005, **17**, 4832.
28 C. H. de Villeneuve, J. Pinson, M. C. Bernard and P. Allongue, *J. Phys. Chem. B*, 1997, **101**, 2415.
29 M. P. Stewart, F. Maya, D. V. Kosynkin, S. M. Dirk, J. J. Stapleton, C. L. McGuiness, D. L. Allara and J. M. Tour, *J. Am. Chem. Soc.*, 2004, **126**, 370.
30 C. Gurtner, A. W. Wun and M. J. Sailor, *Angew. Chem., Int. Ed.*, 1999, **38**, 1966.
31 B. Fabre, G. P. Lopinski and D. D. M. Wayner, *Chem. Commun.*, 2002, 2904.
32 O. Vassylyev, A. Panarello and J. G. Khinast, *Molecules*, 2005, **10**, 587.
33 C. A. Willoughby and S. L. Buchwald, *J. Am. Chem. Soc.*, 1992, **114**, 7562.
34 C. A. Willoughby and S. L. Buchwald, *J. Am. Chem. Soc.*, 1994, **116**, 8952.
35 O. Riant, N. Mostefaï and J. Courmarcel, *Synthesis*, 2004, 2943.
36 X. Verdaguer, U. E. W. Lange and S. L. Buchwald, *Angew. Chem., Int. Ed.*, 1998, **37**, 1103.
37 J. Yun and S. L. Buchwald, *J. Am. Chem. Soc.*, 1999, **121**, 5640.
38 H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger and R. M. Waymouth, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1143.
39 P. C. Mohring and N. J. Coville, *J. Organomet. Chem.*, 1994, **479**, 1.
40 A. Panarello, O. Vassylyev and J. Khinast, *Synlett*, 2005, **5**, 797.
41 H. Gruber-Woelfler, Dissertation, Graz University of Technology, 2007.
42 G. S. Higashi, Y. J. Chabal and G. W. Trucks, *Appl. Phys. Lett.*, 1990, **56**, 656.
43 A. B. Sieval, B. van den Hout, H. Zuilhof and E. J. R. Sudholter, *Langmuir*, 2001, **17**, 2172.
44 A. M. Noskov, *Zh. Prikl. Spektrosk.*, 1968, **10**, 403.
45 G. Socrates, *Infrared and Raman Characteristic Group Frequencies*, Wiley, New York, 3rd edn, 1980.