and benzylamine to yield a mixture of the ketones **6** and **5**.[10, 11] In the case of *tert*-butylethylene (**2a**), only **5a** was isolated (94% yield).

In conclusion, we identified a chelation-assisted, Rh^I-catalyzed *ortho*-alkylation reaction of ketimines with olefins. This type of *ortho*-alkylation shows generality as well as efficiency; the reactions of various olefins (including 1-alkenes, α,ω-dienes, and even internal olefins) with ketimines result in high yields of the corresponding *ortho*-alkylated products. In addition, successive Rh^I-catalyzed hydroacylation and *ortho*-alkylation of an aldehyde gave a product that has been alkylated at two sites.

Experimental Section

Full experimental details can be found in the Supporting Information.

A typical procedure for the preparation of **5a** [Eq. (6)]: A screw-capped pressure vial (1 mL) was charged with freshly purified benzaldehyde (0.216 mmol), 2-amino-3-picoline (**4**, 0.0432 mmol), benzylamine (0.216 mmol), $[Rh(PPh_3)_3Cl]$ (**3**, 0.0216 mmol), and *tert*-butylethylene (**2a**, 1.08 mmol), the mixture was then stirred in an oil bath at 170 °C for 12 h. Purification by column chromatography (SiO_2, *n*-hexane/ethyl acetate = 5/2) gave pure 1-[2-(3,3-dimethyl-butyl)-phenyl]-4,4-dimethyl-pentan-1-one (**5a**) (0.203 mmol, 94% yield).

Received: April 11, 2000 [Z14976]

[1] a) A. D. Ryabov, *Chem. Rev.* **1990**, *90*, 403 – 424; b) A. E. Shilov, G. B. Shul'pin, *Chem. Rev.* **1997**, *97*, 2879 – 2932; c) G. Dyker, *Angew. Chem.* **1999**, *111*, 1808 – 1822; *Angew. Chem. Int. Ed.* **1999**, *38*, 1698 – 1712.

[2] a) C.-H. Jun, H. Lee, J.-B. Hong, *J. Org. Chem.* **1997**, *62*, 1200 – 1201; b) C.-H. Jun, D.-Y. Lee, J.-B. Hong, *Tetrahedron Lett.* **1998**, *38*, 6673 – 6676; c) C.-H. Jun, C.-W. Huh, S.-J. Na, *Angew. Chem.* **1998**, *110*, 150 – 152; *Angew. Chem. Int. Ed.* **1998**, *37*, 145 – 147; d) C.-H. Jun, H.-S. Hong, C.-W. Huh, *Tetrahedron Lett.* **1999**, *40*, 8897 – 8900; e) C.-H. Jun, J.-B. Hong, D.-Y. Lee, *Synlett* **1999**, 1 – 12.

[3] C.-H. Jun, J.-B. Hong, *Org. Lett.* **1999**, *1*, 887 – 889.

[4] a) S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, N. Chatani, *Nature* **1993**, *366*, 529 – 531; b) F. Kakiuchi, Y. Tanaka, T. Sato, N. Chatani, S. Murai, *Chem. Lett.* **1995**, 679 – 680; c) F. Kakiuchi, Y. Yamamoto, N. Chatani, S. Murai, *Chem. Lett.* **1995**, 681 – 682; d) M. Sonoda, F. Kakiuchi, A. Kamatani, N. Chatani, S. Murai, *Chem. Lett.* **1996**, 109 – 110; see also e) C. P. Lenges, M. Brookhart, *J. Am. Chem. Soc.* **1999**, *121*, 6616 – 6623.

[5] a) F. Kakiuchi, S. Sekine, T. Tanaka, A. Kamatani, M. Sonoda, N. Chatani, S. Murai, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 62 – 83; b) S. Murai, N. Chatani, F. Kakiuchi, *Pure Appl. Chem.* **1997**, *69*, 589 – 594

[6] In *ortho*-alkylated ketones, because the unreacted double bond from the α,ω-diene isomerized into an internal olefin, we reduced the double bond to aid isolation and characterization.

[7] M. Sonoda, F. Kakiuchi, N. Chatani, S. Murai, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 3117 – 3128.

[8] a) Y.-G. Lim, Y. H. Kim, J.-B. Kang, *J. Chem. Soc. Chem. Commun.* **1994**, 2267 – 2268; b) Y.-G. Lim, J.-B. Kang, Y. H. Kim, *J. Chem. Soc. Perkin Trans 1* **1996**, 2201 – 2206.

[9] N. A. Williams, Y. Uchimaru, M. Tanaka, *J. Chem. Soc. Chem. Commun.* **1995**, 1129 – 1130.

[10] Recently, we have developed an efficient catalytic system for intermolecular transimination-assisted hydroacylation with aldehydes: C.-H. Jun, D.-Y. Lee, H. Lee, J.-B. Hong, *Angew. Chem.* **2000**, *112*, 3214 – 3216; *Angew. Chem. Int. Ed.* **2000**, *39*, 3070 – 3072.

[11] Without benzylamine, only hydroacylation occurred. The ketimine of 2-amino-3-picoline did not show any *ortho*-alkylation, probably because of the coordination of the Rh^I catalyst to the pyridine moiety.

Microreactors for Dynamic, High Throughput Screening of Fluid/Liquid Molecular Catalysis**

Claude de Bellefon*, Nathalie Tanchoux, Sylvain Caravieilhes, Pierre Grenouillet, and Volker Hessel

Today, high-throughput synthesis methodologies, such as combinatorial techniques, are applied to the discovery of pharmaceuticals, catalysts, and many other new materials.[1, 2] In the near future, huge libraries of ligands, and hence of homogeneous catalyst precursors, will be accessible. Recent reports have demonstrated the effectiveness of this approach for restricted libraries and in the case of catalysis in a single liquid phase.[2] High-throughput screening in one liquid phase should not represent a problem as long as the reactions are not too fast compared with micromixing rates. The microtitration-based apparatus (combinatorial chemistry (CC) factory)[2g] fulfils the requirement of ensuring reproducible tests on microquantities of samples,[2] despite uncertainties attributed to the agitation process.[2b] However, numerous reactions of interest, such as hydrogenation, carbonylation, and hydroformylation, operate in gas/liquid or gas/liquid/liquid systems.[3] Inadequate control of phase and catalyst presentation, a result from nonoptimized agitation, may dramatically affect the estimation of selectivity and reactivity. Many enantio- and regioselective-catalyzed reactions, susceptible to mass transport effects, are known.[4, 5] That may well be the explanation for the deceptively low enantiomeric excess ($ee < 20\%$) obtained in the screening of a 63-member library of rhodium/phosphane catalysts for asymmetric hydrogenation.[2a] Thus, a major challenge is to develop special reactors[1b] for rapid catalyst screening, that would ensure good mass and heat transport in a small volume.[6]

Herein we describe a new concept to achieve high-throughput screening (HTS) of polyphasic fluid reactions. Two test reactions, a liquid/liquid isomerization and a gas/liquid asymmetric hydrogenation, have been chosen to validate our approach to HTS experiments.

As a liquid/liquid test reaction, the isomerization of allylic alcohols, a process currently of industrial interest in the field of geraniol chemistry[7] was targeted [Eq. (1)].

[*] Dr. C. de Bellefon, Dr. N. Tanchoux,[+] S. Caravieilhes, Dr. P. Grenouillet
Laboratoire Génie des Procédés Catalytiques
CNRS/ESCPE Lyon, 69100 Villeurbanne (France)
Fax : (+33) 4-72-43-16-73
E-mail: cdb@lgpc.cpe.fr

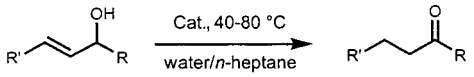
[+] Present address: Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1, 45470 Mülheim a. d. Ruhr (Germany)

Dr. V. Hessel
Institut für Mikrotechnik Mainz
Carl-Zeiss-Strasse 18 – 20, 55129 Mainz (Germany)

[**] This research was funded by the Région Rhône-Alpes, the CNRS, and the Ecole Supérieure de Chimie Physique Electronique de Lyon. S.C. is supported by a grant of the French Ministry of Education. Many thanks to Prof. D. Sinou for a gift of CBDTS.

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

  0044-8249/00/11219-3584 $ 17.50+.50/0



(1)

Biphasic catalytic systems involving organic and aqueous (catalytic) phases, are well known and used in industry.[8] However, whereas numerous reports describe the monophasic isomerization of allylic alcohol,[9] examples of efficient catalysis in biphasic media are scarce.[10] In order to extend the scope of this isomerization to a liquid/liquid system, a restricted library composed of eight catalytic systems was constructed from four transition metal precursors (Rh, Ru, Pd, Ni),[9, 10] and four sulfonated phosphane or diphosphane ligands.

A liquid/liquid HTS test reactor was then designed. Such an apparatus must be able to mix the two liquids with a low to very low inventory of catalytic material while still offering reasonably long residence times.[11] The principle used is a combination of pulse injections of the catalyst and the substrate, a micromixer with negligible volume, and a tubular reactor (Figure 1).

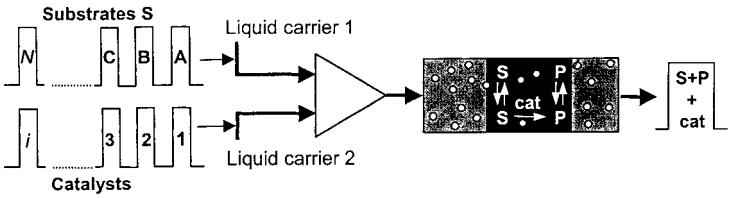


Figure 1. Schematic of the principle used for high-throughput sequential screening of *i* catalysts and *N* substrates. The substrate *S* is thus treated to form the product *P*.

During operation, the two carrier liquid phases, namely *n*-heptane and water, flow continuously through the apparatus. For a test, both the substrate and the catalyst are injected simultaneously. The pulses mix perfectly in the micromixer with a residence time less than 10^{-2} s. The liquids thereby emulsify and behave as a reacting segment, which then travels along the tubular reactor. Collection at the outlet of the reactor and analysis affords the conversion and selectivity data.

Application of this principle has been possible by using a static micromixer[12] mounted in a dynamic microactivity test (Figure 2). The *n*-heptane/water emulsion was stable for more than 10 minutes without noticeable separation.

The catalyst library was then screened (Table 1). Palladium complexes were inactive when associated with monophosphane ligands and displayed a low activity with diphosphane (entries 7 and 8). The use of nickel resulted in a 1,3-transposition of the hydroxy group (entry 9). Ruthenium and rhodium gave comparable conversions. However, the ruthenium catalyst yields some hydrogenated side product due to hydride transfer from the alcohol (entry 6). Different precursors of rhodium(I) were active (entries 1 and 2) and comparable conversions were measured with mono- and diphosphane ligands (entries 1–5). These results led to the selection of Rh/TPPTS as the best catalyst.

This selected $RhCl_3$/TPPTS catalyst showed activity towards a large class of allylic alcohols (Figure 3).

That similar results were obtained in the microreactor and in a traditional well mixed batch reactor (40 cm^3) proves the validity of the concept. Differences observed between the substrates are explained by both their different solubilities in the catalytic layer and by their different intrinsic reactivities. Thus, substrates **1**–**4**, which are likely to possess similar reactivities, displayed a decreasing conversions with an increasing hydrocarbon chain length. The molecular structure of the substrate is also of importance: For similar solubilities, **1** is more reactive than **5**, **2** more than **6**, and **3** more than **7** and **8** for the C_4, C_5, and C_6 compounds, respectively. This pairwise

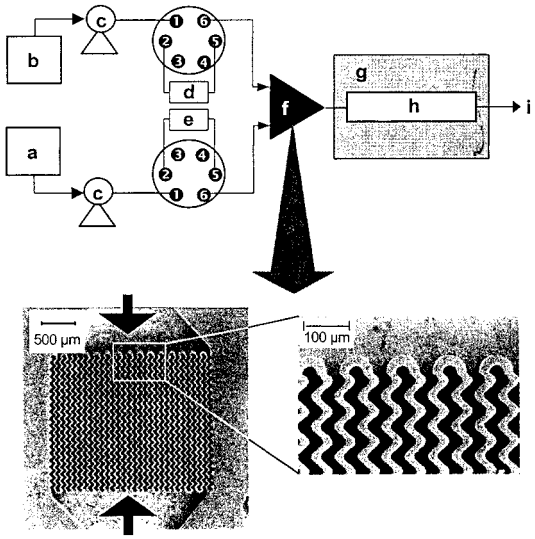
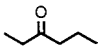
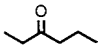
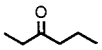
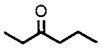
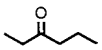
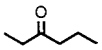
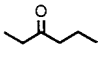
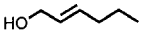
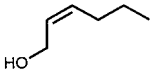


Figure 2. Appartus: a) water reservoir; b) *n*-heptane reservoir; c) high-pressure liquid pumps; d) injection valve with a 200 µL loop; e) injection valve with a 1 mL loop; f) micromixer; g) thermoregulated bath; h) tubular stainless-steel reactor (0.4 cm i.d., 80 cm long); i) outlet to detectors. The two scanning electron microscopy (SEM) images show the micromixer, in which the 2×15 interdigitated microchannels (25 µm width) with corrugated walls are clear.

Table 1. Screening of catalysts for the isomerization of 1-hexene-3-ol.

Entry	Catalyst[a]	Ligand:metal	Product	Conv. [%][b]
1	$RhCl_3$/TPPTS	4.6:1		53
2	Rh_2SO_4/TPPTS	4.1:1		34
3	$[Rh(cod)Cl]_2$/DPPBTS	1.1:1		36
4	$[Rh(cod)Cl]_2$/BDPPTS	1.1:1		1.5
5	$[Rh(cod)Cl]_2$/CBDTS	1.3:1		1
6	$RuCl_3$/TPPTS	4:1		61
7	$PdCL_2$/DPPBTS	2.6:1		3.5
				9
8	$Ni(cod)_2$/TPPTS	4:1		3

[a] All catalysts were prepared separately beforehand and stored under argon at 4 °C.[10c] [b] Gas chromatography analysis. TPPTS = tris(*m*-sulfophenyl)phosphane, cod = cycloocta-1,4-diene, DPPBTS = di(sulfophenylphosphanyl)butane, BDPPTS = sulfonated (2*S*,4*S*)-(−)-2,4-bis(diphenylphosphanyl)pentane, CBDTS = sulfonated (S,S)-1,2-bis(diphenylphosphanylmethyl)cyclobutane.

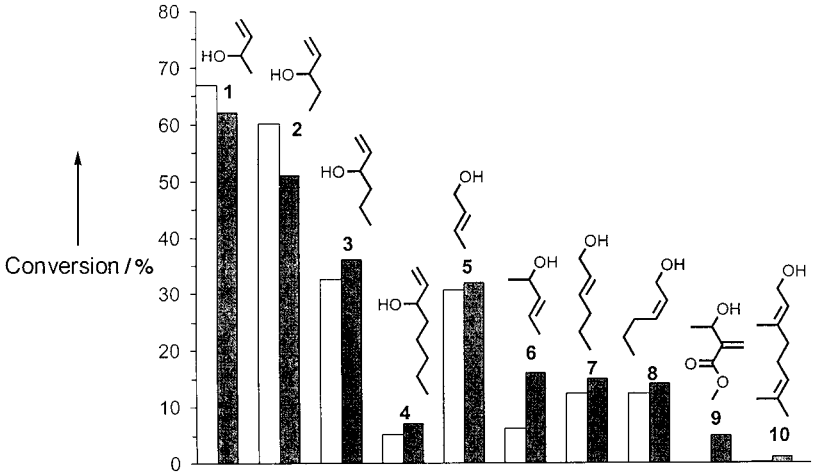


Figure 3. Comparison between the results of the screening of substrates **1**–**10** against one catalyst in a traditional batch reactor (white columns) and in the micro-dynamic test (gray columns). The catalyst pulse was 200 μL and [Rh] = 4 mM, other conditions are given in the Experimental Section.

comparison leads to the known conclusion that secondary alcohols with terminal olefins are more reactive than other configurations.[9a] All these results are in good agreement with those reported for monophasic systems and further validates the use of the microapparatus for chemical investigations.

The concept has been extended to gas/liquid catalysis with some modification to the experimental setup. Thus, hydrogen is introduced at one of the inlet of the micromixer and the liquid carrier phase is pumped into the other. The liquid, ethylene glycol/water (60/40 wt %) and sodium dodecyl sulfate (SDS) surfactant, is thus composed to ensure a stable foam (no coalescence was noticed for residence times up to 6 min at 60 °C) with small gas bubles (about 200 μm average diameter) with a liquid volume of 20 %. A pulse containing the substrate *Z*-(α)-acetamidocinamic methyl ester (MAC; 0.05–0.10 M) and the Rh/diphos catalyst (diphos ligands are *S*,*S*-CBDTS and *S*,*S*-BDPPTS) dissolved in the liquid mixture is injected. Using this procedure, we have found that the rate of reaction is proportional to the catalyst concentration and that the rate decreases with increasing SDS concentration, but no change in the *ee* was noticed (see Supporting Information for details). These results indicate strongly that the microreactor is working under a chemical regime. A further argument comes from the comparison of the enantioselectivities obtained in the microreactor and those previously reported for the catalysts Rh/*S*,*S*-CDBTS (*ee* 6 % versus 20 % (*S*)) and Rh/(*S*,*S*)-BDPPTS (*ee* 47 % versus 45 % (*R*)) under similar conditions.[13]

In terms of catalyst and time consumption per test, the 18 tests for the liquid/liquid isomerization (Table 1 and Figure 3) were performed twice, to test for reproducibility, using one to two micromoles of metal and over a total screening time of one hour. The test for the the gas/liquid asymmetric hydrogenation showed similar features (down to 0.2 μmol Rh, 3–5 min per test). Throughput testing frequencies (TTFs) of more than 500 d^{-1} are thus achievable, albeit with computer control of the apparatus.

Such TTFs impose a characteristic time of about only 3 min for necessary online operations, such as injection, collection, and analysis. The latter operation is often the rate-limiting step in combinatorial and related techniques. With the dynamic sequential method proposed here, any detectors that were originally designed for HPLC or GC analysis may be used, which includes mass detection, UV, IR, CD, and so forth. Fast chromatography with microcapillary columns is also possible (see the Supporting Information).

In summary, we propose a new concept for high-throughput experiments based on dynamic sequential operations with a combination of pulse injections and micromachined elements. Some advantages over traditional parallel batch operations are reduced sample amounts (to μg levels), a larger range of operating conditions (pressure, temperature), and fewer, simpler electro-mechanical moving parts.

Experimental Section

Liquid/liquid isomerization: Aqueous catalyst solution pulses (200 μL), which contain about 1–2 μmol (about 100 μg) of metal, and organic substrate pulses (1 mL), as *n*-heptane solutions (0.1 mol L^{-1}), were used for each test. Flow rates were 5 (aqueous phase) and 1 mL min^{-1} (organic phase), which corresponded to a residence time of 100 s in the stainless-steel tubular reactor (0.4 × 80 cm) that was maintained at 80 °C.

Gas/liquid asymmetric hydrogenation: Aqueous catalyst solution pulses (200 μL), which contain about 1–4 mM of the catalyst, and organic substrate pulses of MAC (0.05–0.10 M) were used for each test. Flow rates were 1–4 mL min^{-1} (gas phase) and 0.3–1.0 mL min^{-1} (liquid phase), which corresponded to a residence time of 3–6 min in the tubular glass reactor (0.285 × 156 cm), that was maintained at atmospheric pressure and at 40–60 °C.

Received: April 12, 2000
Revised: June 9, 2000 [Z14979]

[1] a) B. Jandeleit, D. J. Schaefer, T. S. Powers, H. W. Turner, W. H. Weinberg, *Angew. Chem.* **1999**, *111*, 2648; *Angew. Chem. Int. Ed.* **1999**, *38*, 2494; b) R. H. Crabtree, *CHEMTECH* **1999**, *29* (*4*), 21; c) T. Bein, *Angew. Chem.* **1999**, *111*, 335; *Angew. Chem. Int. Ed.* **1999**, *38*, 323; d) D. R. Liu, P. G. Schultz, *Angew. Chem.* **1999**, *111*, 36; *Angew. Chem. Int. Ed.* **1999**, *38*, 36.

[2] a) S. R. Gilbertson, X. Wang, *Tetrahedron Lett.* **1996**, *36*, 6475; b) K. Burgess, H.-J. Lim, A. M. Porte, G. A. Sulikowski, *Angew. Chem.* **1996**, *108*, 192; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 220; c) M. B. Francis, N. S. Finney, E. N. Jacobsen, *J. Am. Chem. Soc.* **1996**, *118*, 8983; d) K. D. Shimizu, M. L. Snapper, A. H. Hoveyda, *Chem. Eur. J.* **1998**, *4*, 1885; e) D. A. Annis, O. Helluin, E. N. Jacobsen, *Angew. Chem.* **1998**, *110*, 2010; *Angew. Chem. Int. Ed.* **1998**, *37*, 1907; f) M. T. Reetz, M. H. Becker, K. M. Kühling, A. Holzwarth, *Angew. Chem.* **1998**, *110*, 2792; *Angew. Chem. Int. Ed.* **1998**, *37*, 2647; g) K. Ding, A. Ishii, K. Mikami, *Angew. Chem.* **1999**, *111*, 2268; *Angew. Chem. Int. Ed.* **1999**, *38*, 497; h) M. B. Francis, E. N. Jacobsen, *Angew. Chem.* **1999**, *111*, 987; *Angew. Chem. Int. Ed.* **1999**, *38*, 937; i) O. Lavastre, J. P. Morken, *Angew. Chem.* **1999**, *111*, 3357; *Angew. Chem. Int. Ed.* **1999**, *38*, 3163.

[3] B. Cornils, W. A. Herrmann, *Applied Homogeneous Catalysis with Organometallic Compounds*, VCH, Weinheim, **1996**.

[4] a) C. R. Landis, J. Halpern, *J. Am. Chem. Soc.* **1987**, *109*, 1746; b) R. V. Gholap, O. M. Kut, J. R. Bourne, *Ind. Eng. Chem. Res.* **1992**, *31*, 2446; c) N. Tanchoux, C. de Bellefon, *Tetrahedron: Asymmetry* **1998**, *9*, 3677.

[5] Y. Sun, R. N. Landau, J. Wang, C. Le Blond, D. G. Blackmond, *J. Am. Chem. Soc.* **1996**, *118*, 1348.

  0044-8249/00/11219-3586 $ 17.50+.50/0

[6] Computer-controlled apparatus with mixing and pressure handling capabilities are known. They are based on the concept of operating of traditional laboratory "glassware" procedures in parallel at a miniature scale and function batchwise with throughput testing frequencies (TTFs) of 10–40 day^{-1}. Mechanical mixing is the bottleneck for further miniaturization. Some information is available at www.ttpmyriad.co.uk, www.argotech.com, www.peptide.com, and www.gilson.com.
[7] S. Otsuka, T. Kazuhide, *Synthesis* **1991**, *9*, 665.
[8] B. Cornils, E. G. Kuntz in *Aqueous-Phase Organometallic Catalysis* (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, Weinheim, **1998**, p. 271.
[9] a) Y. Sasson, G. L. Rempel, *Tetrahedron Lett.* **1974**, *47*, 4133; b) K. Felfödi, M. Bartòk, *J. Organomet. Chem.* **1985**, *297*, 37; c) B. M. Trost, R. J. Kulawiec, *Tetrahedron Lett.* **1991**, *32*, 3039; d) I. E. Marko, A. E. Gautier, M. Tsukazaki, A. Llobet, E. Plantalech-Mir, C. J. Urch, S. M. Brown, *Angew. Chem.* **1999**, *111*, 2126; *Angew. Chem. Int. Ed.* **1999**, *38*, 1960.
[10] a) H. Schumann, V. Ravindar, L. Meltser, W. Baidossi, Y. Sasson, J. Blum, *J. Mol. Catal. A* **1997**, *118*, 55; b) H. Bricout, E. Monflier, J. F. Carpentier, A. Mortreux, *Eur. J. Inorg. Chem.* **1998**, 1739; c) C. de Bellefon, S. Caravieilhes, E. G. Kuntz, *C. R. Acad. Sci. Ser. 2*, in press.
[11] C. de Bellefon, S. Caravieilhes, N. Tanchoux *J. Organomet. Chem.* **1998**, *567*, 143.
[12] a) W. Ehrfeld, K. Golbig, V. Hessel, H. Löwe, T. Richter, *Ind. Eng. Chem. Res.* **1999**, *38*, 1075; b) H. Löwe, W. Ehrfeld, V. Hessel, T. Richter, J. Schiewe, *Proc. 4th Int. Conf. Microreaction Technology* (Atlanta, GA, USA) **2000**.
[13] Y. Amrani, L. Lecomte, D. Sinou, J. Bakos, I. Toth, B. Heil, *Organometallics* **1989**, *8*, 542.

Macromolecular-Multisite Catalysts Obtained by Grafting Diaminoaryl Palladium(II) Complexes onto a Hyperbranched-Polytriallylsilane Support**

Christian Schlenk, Arjan W. Kleij, Holger Frey,* and Gerard van Koten*

At present, dendrimers[1] are widely investigated as supports for catalytically active transition metal fragments.[2] Carbosilane dendrimers[3] are well-suited for this purpose, because they are relatively inert to common organometallic reagents and their structures can be easily modified. The main advantage of this type of nanosized, macromolecular catalyst is their convenient removal from product streams as realized recently in a continuously operating membrane reactor.[4] However, the synthesis of dendrimers, that is monodisperse, well-defined molecules, involves expensive, labor-intensive multistep procedures that also limit the amount of available material. In contrast, hyperbranched polymers[5] can be prepared in a single-step, one-pot procedure, from AB_m type monomers. This greatly facilitates their synthesis and allows the production of large quantities of material. However, as a consequence of the uncontrolled synthesis of such polymers, materials with high polydispersity are obtained. Furthermore, the reactive sites introduced by functionalization will be distributed throughout the molecules.

Recently, we reported carbosilane molecules functionalized with NCN $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$) ligands[6, 7] which could then be selectively lithiated without any decomposition of the carbosilane backbone.[8] This lithiation enabled the subsequent incorporation of transition metals by means of transmetalation with suitable Group 8 metal salts.[2a, 8b] Herein, we present the synthesis of a hyperbranched carbosilane (HCS), its functionalization with NCN moieties, and the introduction of palladium(II) sites into the structure. Furthermore, we show that this system can be conveniently converted into an effective catalyst system that can compete with metallodendritic catalysts.

To obtain hyperbranched HCS supports, neat triallylsilane[9] was polymerized with platinum catalysis by polyaddition (Scheme 1).[10] To keep the isomerization of the double bonds to a minimum, the reaction temperature was kept low (40 °C). This, however, led to prolonged reaction times (4 d in the case of **1**). The internal to external double-bond ratio could not be suppressed below 7.6 %. The presence of internal double bonds was indicated in the ^{1}H NMR spectrum of the isolated HCS material which showed the presence of extra multiplets at $\delta = 6.09$ ($SiCH{=}C\mathit{H}\text{-}CH_3$) and 5.58 ($SiC\mathit{H}{=}CH\text{-}CH_3$). The polytriallylsilane (PTAS) **1**, was obtained as a translucent, viscous oil, soluble in solvents such as diethyl ether and chloroform. The molecular weight (size exclusion chromatography (SEC), polystyrene (PS) standards was 5500 $g\,mol^{-1}$ which corresponds to an apparent degree of polymerization of 36 (that is 72 allyl groups per molecule). As expected for a bulk polymerization of an AB_m monomer, the molecular-weight distribution was broad ($M_w/M_n = 5.2$).[11] This polydispersity is also influenced by an intramolecular reaction, of the Si–H groups with allyl end groups. This side reaction consumes Si–H groups without enhancement of the molecular weight, resulting in the formation of core-type molecules.

Polymer **1** was hydrosilylated with $HSiMe_2Cl$ by platinum catalysis (Scheme 1) in neat $HSiMe_2Cl$ at ambient temperature. After removal of the excess $HSiMe_2Cl$, the functionalized polymer HCS-$SiMe_2Cl$ (**2**) was dissolved in diethyl ether. This solution was added to 3,5-bis[(dimethylamino)-methyl] phenyllithium (Li-NCN)[8a] at −78 °C in diethyl ether (Scheme 2). Hydrolysis followed by extraction gave the crude HCS-$SiMe_2$-NC(H)N product. This diaminoaryl-functional-

[*] Prof. Dr. G. van Koten, A. W. Kleij
Debye Institute
Department of Metal-Mediated Synthesis
Utrecht University
Padualaan 8, 3584 CH, Utrecht (The Netherlands)
Fax: (+31) 30-252-3615
E-mail: g.vankoten@chem.uu.nl
PD Dr. H. Frey, C. Schlenk
Freiburger Materialforschungszentrum und Institut für Makromolekulare Chemie
Albert-Ludwigs-Universität, Freiburg
Stefan-Meier-Strasse 21/31, 79104 Freiburg (Germany)
Fax: (+49) 761-203-6319;
E-mail: holfrey@fmf.uni-freiburg.de

[**] We thank the Council for Chemical Sciences (CW) of the Netherlands Organization of Scientific Research (NWO) for financial support, Dr. R. Hanselmann for the size exclusion chromatography (SEC) measurements, and Dr. J. Boersma for critical reading of the manuscript.

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.