by Arigoni et al. in the dehydration by dioldehydrase (J. Rétey, A, Umani-Ronchi, J. Seibl, D. Arigoni, *Experientia* **1966**, *22*, 502). It should also be noted that the possibility of dehydration occurring prior to a complete conformational equilibration of the formed *gem*-diol and leading to the release of the newly incorporated ^{18}O atom cannot be ruled out based on our current data.

[14] Attempts to derivatize the diethyl ester **9** with various chiral acids to resolve the racemic mixture were futile.

[15] I. Ohtani, T. Kusumi, Y. Kashman, H. Kakisawa, *J. Am. Chem. Soc.* **1991**, *113*, 4092 – 4096.

[16] The incubation conditions were similar to those in ref. [8]. Spectral data of **12** in the keto form (74 %): ^1H NMR (D_2O): $\delta = 2.29$ ppm (s, 3H); ^{19}F NMR (D_2O): $\delta = -118.59$ ppm (d, $J = 77.8$ Hz); ^{31}P NMR (D_2O): $\delta = 2.90$ (t, $J = 76.0$ Hz); high resolution MS (CI) calcd for $C_3H_6F_2PO_4$ [M^++H]: m/z: 174.9972, found 174.9979. Spectral data of **12** in the hydrate form (26 %): ^1H NMR (D_2O): $\delta = 1.32$ ppm (s, 3H); ^{19}F NMR (D_2O): $\delta = -124.17$ ppm (d, $J = 79.8$ Hz); ^{31}P NMR (D_2O): $\delta = 5.69$ ppm (t, $J = 79.0$ Hz); high resolution MS (CI) calcd for $C_3H_8F_2PO_5$ [M^++H]: m/z: 193.0077, found 193.0072.

[17] Recent examples of adjacent carbanion formation triggering fluoride release: a) J. W. Gross, A. D. Hegeman, B. Gerratana, P. A. Frey, *Biochemistry* **2001**, *40*, 12497 – 12504; b) C. W. Koo, A. Sutherland, J. C. Vederas, J. S. Blanchard, *J. Am. Chem. Soc.* **2000**, *122*, 6122 – 6123.

[18] The possible involvement of a ketyl radical in the turnover of (*R*)-**1** and (*R*)-**8** is reminiscent of the mechanism of the oxidation of primary alcohols catalyzed by galactose oxidase (M. M. Whittaker, D. P. Ballou, J. W. Whittaker, *Biochemistry* **1998**, *37*, 8426 – 8436; B. E. Turner, B. P. Branchaud, *Bioorg. Med. Chem. Lett.* **1999**, *9*, 3341 – 3346).

[19] Two recent examples include the conversion of (1*S*,2*R*)- and (1*R*,2*S*)-*trans*-1-methyl-2-phenylcyclopropane into a primary alcohol and a phenol, respectively, by methane monooxygenase from *Methylococcus capsulatus* (A. M. Valentine, M.-H. LeTadic-Biadatti, P. H. Toy, M. Newcomb, S. J. Lippard, *J. Biol. Chem.* **1999**, *274*, 10771 – 10776), and the oxidation of 2-ethylhexanol by cytochrome $P450_{cam}$ in which 2-ethylhexanoic acid and 2-ethyl-1,2-hexanediol, respectively, are derived from the *R* and *S* isomer as the major product (K. J. French, D. A. Rock, D. A. Rock, J. I. Manchester, B. M. Goldstein, J. P. Jones, *Arch. Biochem. Biophys.* **2002**, *398*, 188 – 197).

[20] A recent report has shown that the (1*S*,2*S*)-epoxypropylphosphonic acid exists as a co-metabolite of fosfomycin ((1*R*,2*S*)-epoxypropylphosphonic acid, **2**) in the culture broth of *Streptomyces fradiae*. Formation of this 1*S* epimer has been speculated as a result of racemization of the radical intermediate (such as **4** or its equivalent) generated during turnover catalyzed by HPP epoxidase (B. P. Simov, F. Wuggenig, M. Lämmerhofer, W. Lindner, E. Zarbl, F. Hammerschmidt, *Eur. J. Org. Chem.* **2002**, 1139 – 1142).

Novel Achiral Biphenol-Derived Diastereomeric Oxovanadium(IV) Complexes for Highly Enantioselective Oxidative Coupling of 2-Naphthols**

Zhibin Luo, Quanzhong Liu, Liuzhu Gong,* Xin Cui, Aiqiao Mi, and Yaozhong Jiang

Optically pure 1,1′-binaphthol and its derivatives have been evaluated as versatile chiral auxiliaries and ligands in asymmetric transformations. Research in this area has provided many efficient and useful methods for the preparation of key chiral building blocks, some of which have been used for the construction of complex natural products.[1] They have also been extensively applied to the preparation of chiral organic materials.[2] The wide-ranging and important applications of such compounds in organic synthesis have stimulated great interest in developing efficient methods for their preparation.[3] Compared to the well-established resolution of racemic binaphthol for the preparation of optically pure BINOL,[3a–f] catalytic asymmetric preparation of chiral binaphthols has developed much more slowly. The discovery of efficient catalysts for the highly enantioselective formation of optically active binaphthol and its derivatives is an attractive target. The oxidative coupling of 2-naphthols in the presence of a catalytic amount of a copper complex of a chiral amine has provided several promising results, but high enantioselectivity has been achieved only for the coupling of 3-carboalkoxyl-2-naphthols (93 % *ee*).[4] A photo-activated chiral [Ru^{II}(salen)(NO)] complex catalyzes the aerobic oxidative coupling of 2-naphthols with 33–71 % *ee*.[5] Chen et al. and Uang et al. independently designed similar oxovanadium(IV) complexes of chiral Schiff bases for the asymmetric oxidative coupling of 2-naphthols with moderate enantioselectivities of up to 62 % *ee*.[6]

We developed the catalyst (*R*,*S*)-**1c** for the oxidative coupling of 2-naphthol with high enantioselectivity, and found that the chiral centers on the amino acid part and the axially chiral binaphthyl unit are both crucial to stereocontrol by the catalyst.[7] However, a drawback is that the chiral oxovanadium complex must be prepared from an optically pure 3,3′-diformyl-2,2′-dihydroxy-1,1′-binaphthol and (*S*)-amino acid. The catalyst is only highly enantioselective when the two

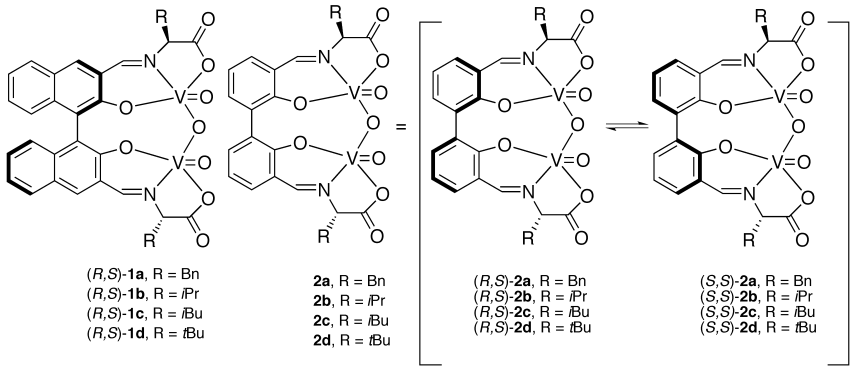
[*] Prof. L. Gong, Z. Luo, Q. Liu, X. Cui, Prof. A. Mi, Y. Jiang
Union Laboratory of Asymmetric Synthesis
Chengdu Institute of Organic Chemistry
Chinese Academy of Sciences
Chengdu, 610041 (P.R. China)
Fax: (+86) 28-8522-3978
E-mail: gonglz@cioc.ac.cn

[**] We are grateful for financial support from the National Science Foundation of China (20102005). We thank Prof. Lin Pu at the University of Virginia for helpful discussions and English revision. We also thank Prof. Nengyu Chen at Lanzhou University for HRMS measurements.

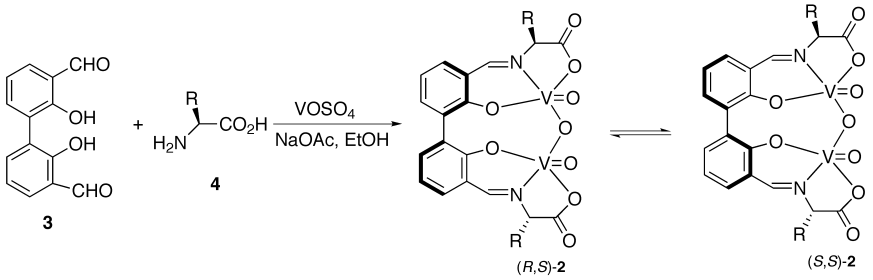
Supporting information for this article (general procedures for the preparation of chiral oxovanadium catalysts and asymmetric couplings of 2-naphthols; HRMS spectra of **2a–d**; HPLC spectra of **6a–c**, **6e**, and **6g–k**) is available on the WWW under http://www.angewandte.org or from the author.

  0044-8249/02/4123-4532 $ 20.00+.50/0

chiral strucutres match; for example, both (*R*,*S*)-**1a** and (*S*,*S*)-**1a** show similar reactivity, but (*R*,*S*)-**1a** gives much higher enantioselectivity than (*S*,*S*)-**1a**.[7] Oxovanadium(IV) complexes **2** are structurally similar to **1**, except that the binaphthyl unit of **1** is replaced with a conformationally flexible biphenyl unit (Scheme 1). In principle, diastereomeric complexes will be generated when 3,3′-diformyl-2,2′-dihydroxy-1,1′-phenol (**3**)[8] is condensed with (*S*)-amino acids **4** and vanadyl sulfate because of the higher rotation barrier in **2** (Scheme 2).[9] We anticipated that the diastereomers with



Scheme 1. Catalysts evaluated in this study.



Scheme 2. Preparation of catalysts **2**.

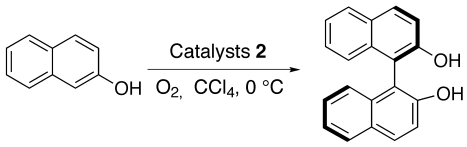
matching chirality between the chiral centers of the amino acid unit and the induced axially chiral biphenyl unit should provide high enantioselectivity for oxidative coupling. This system, which dispenses with the use of optically pure 1,1′-binaphthyls, should have significant practical advantages over the chiral binaphthyl-based catalysts (*R*,*S*)-**1**. Here we present our work on this new type of catalysts for the asymmetric synthesis of 1,1′-binaphthols.

Oxovanadium complexes **2** were prepared by condensation of **3** with (*S*)-amino acids **4** and vanadyl sulfate (Scheme 2) according to the previously reported procedure.[7,10] Preliminary characterization of complexes **2** by HRMS, IR spectroscopy, and elemental analysis supported the structures. These complexes possibly exist as mixtures of diastereomers. Although it is difficult to separate these and determine their absolute structures at this stage, the mixtures of diastereomers were found to be efficient for the asymmetric oxidative coupling of 2-naphthols.

The oxidative coupling of 2-naphthol was employed as a model reaction to investigate the effects of the substituents of the amino acids and the catalyst loading on reactivity and enantioselectivity (Table 1). The reactions to examine substituent effects were carried out in the presence of 10 mol % of **2** in CCl_4 at 0 °C with molecular oxygen as oxidant. Both the reactivity and enantioselectivity are dependent on the substituent R of the amino acids. Complex **2a**, derived from (*S*)-phenylalanine, gives a yield of 77 % and a moderate enantioselectivity of 80 % *ee* (entry 1). Replacement of the phenyl group in **2a** with an isopropyl substituent (**2b**) results in a much lower yield of 42 % and an *ee* value of 79 % (entry 2). Catalyst **2d** bearing bulky *tert*-butyl groups leads to 79 % *ee* and 56 % yield (entry 4). The highest yield of 89 % and an *ee* value of 89 % were observed for catalyst **2c** (R = 2-butyl, entry 3). Lowering the catalyst loading of **2c** does not affect the enantioselectivity, but lowers the reaction rate and yield (entries 6–8). Even in the presence of 1 mol % **2c**, good enantioselectivity is still obtained (entry 8). To our knowledge, these results represent the most enantioselective catalytic coupling of 2-naphthol. More importantly, most of these newly designed catalysts **2**, even though employed as mixtures of diastereomers, still give higher or comparable enantioselectivities in comparison with their 1,1′-binaphthyl analogues (*R*,*S*)-**1**.[7] These results imply that the major diastereomers in **2** might have an axial chirality similar to that of the 1,1′-binaphthyl unit of *(R,S)*-**1**, which matches the chirality of the (*S*)-amino acid unit and controls the stereodiscrimination.

We also prepared the C_1-symmetric complex **2e**, and characterized its structure preliminarily by HRMS and IR specroscopy. Under optimal reaction conditions, only 40 % yield and 57 % *ee* were obtained in the oxidative coupling of 2-

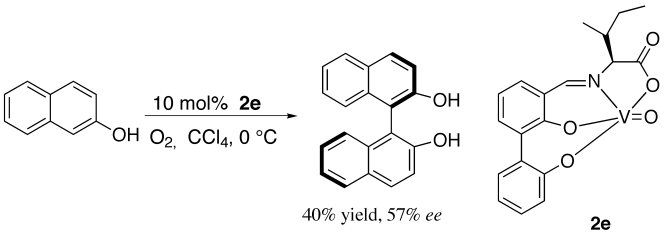
Table 1. Oxidative coupling of 2-naphthol in the presence of oxovanadium complexes **2**.[a]



Entry	Catalyst	R	Cat. load [mol %]	*t* [c]	Yield [%][b]	*ee* [%][c]
1	**2a**	Bn	10	7	77	80
2	**2b**	*i*Pr	10	7	42	79
3	**2c**	*i*Bu	10	7	89	89
4	**2d**	*t*Bu	10	7	56	79
5	(*R*,*S*)-**1c**	*i*Bu	10	8	93	83[d]
6	**2c**	*i*Bu	5	7	62	90
7	**2c**	*i*Bu	2	7	60[e]	91
8	**2c**	*i*Bu	1	7	20[e]	89

[a] Reactions were performed in CCl_4 at 0 °C. [b] Yields of isolated products. [c] The *ee* values were determined by HPLC on a Kromasil CHI-TBB column, and the absolute configuration is *R*. [d] See ref. [7]. [e] Conversion was determined by HPLC.

  0044-8249/02/4123-4533 $ 20.00+.50/0



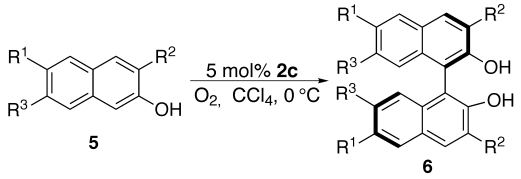
Scheme 3. Oxidative coupling of 2-naphthol in the presence of **2e**.

naphthol (Scheme 3). This demonstrates that the C_2 symmetry of complexes **2a–d** is important for asymmetric induction, and also indicates that the axial chirality induced by the (*S*)-amino acid exists in complexes **2a–d** and is crucial for the enantioselectivity.[9]

The optimized protocol was subsequently extended to a range of substrates (Table 2). For substrates bearing substituents in the 6- or 7-position, coupling takes place smoothly to give the corresponding binaphthols in high yields and 90–97% *ee*. Catalyst **2c** gave higher enantioselectivities for 7-substituted 2-naphthols (entries 3, 6, 8–12) than for 6-bromo-2-naphthol (entry 4) and 2-naphthol itself (entry 1). The enantioselectivity does not depend on the size of the substituents. Variation of the substituent at C7 from methoxy to other alkoxy groups hardly changed the enantioselectivity. Substitution at C3 of 2-naphthol suppresses the coupling reactivity for this catalyst system (entries 5 and 7), and this is similar to the results obtained with (*R*,*S*)-**1c**.[7]

We have further extended our study on the previously reported catalyst **1c**.[7] Table 3 summarizes the results of **1c**-catalyzed oxidative coupling of 2-naphthol derivatives.

Table 2. Oxidative coupling of 2-naphthols in the presence of 5 mol% oxovanadium(IV) complex **2c**.[a]



Entry	Products	Substituentes in **6**	*t* [days]	Yield [%][b]	*ee* [%][c]
1	**6a**	$R^1=R^2=R^3=H$	8	62	90
2	**6a**	$R^1=R^2=R^3=H$	7	89	89[d]
3	**6b**	$R^1=R^2=H$, $R^3=OMe$	7	95	95
4	**6c**	$R^1=Br$, $R^2=R^3=H$	4	98	90
5	**6d**	$R^1=H$, $R^2=OMe$, $R^3=H$	6	trace	–
6	**6e**	$R^1=R^2=H$, $R^3=OEt$	4	99	96
7	**6f**	$R^1=H$, $R^2=OBn$, $R^3=H$	6	trace	–
8	**6g**	$R^1=R^2=H$, $R^3=OBn$	6	80	95
9	**6h**	$R^1=R^2=H$, $R^3=O$*n*Bu	4	99	94
10	**6i**	$R^1=R^2=H$, $R^3=OCH_2CH{=}CH_2$	4	99	95
11	**6j**	$R^1=R^2=H$, $R^3=OC_8H_{17}$	4	99	94
12	**6k**	$R^1=R^2=H$, $R^3=OC_{12}H_{25}$	4	94	97

[a] The reactions were carried out at 0°C in the presence of 5 mol% catalyst **2c** in CCl_4. [b] Yields of isolated products. [c] The *ee* values were determined by HPLC on a Kromasil CHI-TBB or chiralpak AD column, the configuration of **6a–c** is *R*. [d] In the presence of 10 mol% **2c**.

Table 3. Oxidative coupling of 2-naphthols in the presence of 10 mol% oxovanadium(IV) complex **1c**.[a]

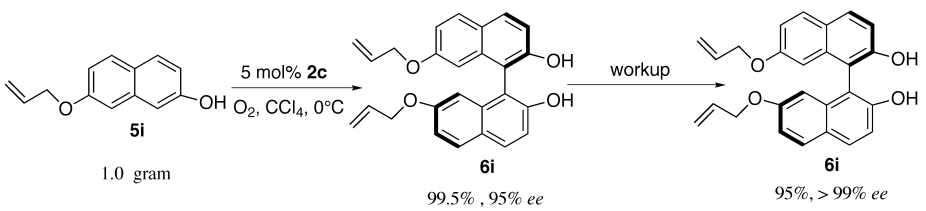
Entry	Products	*t* [days]	Yield [%][b]	*ee* [%][c]
1	**6a**	8	95	83[d]
2	**6b**	7	88	98[d]
3	**6c**	7	99	88[d]
4	**6e**	7	99	93
5	**6h**	7	95	96
6	**6i**	7	98	95
7	**6j**	7	93	94
8	**6k**	7	91	92

[a] The reactions were carried out at 0°C in the presence of 10 mol% catalyst **1c** in CCl_4. [b] Yields of isolated products. [c] The *ee* values are determined by HPLC on a Kromasil CHI-TBB or chiralpak AD column, the configuration of **6a–c** is *R*. [d] From ref. [7].

This complex exhibits almost the same enantioselectvity as **2c** for most of the 7-alkoxynaphthols, with 92–98% *ee* (Table 3, entries 2 and 4–8), while **2c** provides 94–97% *ee* (Table 2, entries 3, 6, and 8–12). Generally, **2c** gives a slightly higher enantioselectivity with 2-naphthol (90% *ee*, Table 2, entry 1) and 6-bromo-2-naphthol (90% *ee*, Table 2, entry 4) than (*R*,*S*)-**1c** (Table 3, entries 1 and 3).[7] Remarkably, when the optically pure binaphthyl catalysts are replaced with the achiral biphenol-derived mixtures of diastereomers, oxidative coupling still occurs with high enantioselectvity. Complexes **2c** and (*R*,*S*)-**1c** represent the most enantioselective catalysts for the catalytic oxidative coupling of 2-naphthols, and, together with the results of Kozlowski et al.,[4b] will provide a practical way to prepare optically active binaphthols catalytically.

As a test of the practicality, oxidative coupling of **5i** in the presence of 5 mol% of catalyst **2c** was scaled up to 1.0 g, and gave **6i** with 95% *ee* and nearly quantitive yield, similar to the result obtained on a small scale (Scheme 4). After purification, **6i** was obtained as a sticky oil with over 99% *ee* and 95% yield. It can be transformed into many useful chiral ligands by modification through several known reaction sequences.

In summary, we have presented the most enantioselective catalytic oxidative coupling of 2-naphthols by a series of novel achiral biphenol-derived diastereomeric oxovanadium(IV)



Scheme 4. Asymmetric, catalytic preparation of optically pure **6i** on a large scale.

  0044-8249/02/4123-4534 $ 20.00+.50/0 *Angew. Chem. Int. Ed.* **2002**, *41*, No. 23

complexes **2**. In the presence of 5 mol % of the best catalyst **2c**, excellent enantioselectivities of 90–97 % *ee* and high yields were obtained for nine 2-naphthols. Compared with its structural analogue (*R*,*S*)-**1c**, which contains an optically pure 1,1′-binaphthyl unit, **2c**, despite its conformationally flexible biphenyl unit, still exhibits comparable or higher enantioselectivities. This discovery not only provides practical catalysts for the asymmetric synthesis of 1,1′-binaphthols but is also of significant fundamental interest.

Received: July 12, 2002 [Z19726]

[1] For reviews, see a) R. Noyori, *Asymmetric Catalysis in the Organic Synthesis*; Wiley, New York, **1994**; b) R. Noyori, H. Takaya, *Acc. Chem. Res.* **1990**, *23*, 345; c) *Comprehensive Asymmetric Catalysis* (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, Berlin, **1999**; d) K. A. Jørgensen, *Angew. Chem.* **2000**, *112*, 3702; *Angew. Chem. Int. Ed.* **2000**, *39*, 3558; e) C. Bolm, J. P. Hildebrand, K. Muniz, N. Hermanns, *Angew. Chem.* **2001**, *113*, 3382; *Angew. Chem. Int. Ed.* **2001**, *40*, 3284.

[2] For reviews, see a) L. Pu, *Chem. Rev.* **1998**, *98*, 2405; for leading representative research, see b) M. Irie, T. Yorozu, K. Hayashi, *J. Am. Chem. Soc.* **1978**, *100*, 2236; c) T. D. James, K. R. A. S. Sandanayke, S. Shinkai, *Nature* **1995**, *374*, 345; d) K. Akagi, G. Piao, S. Kaneko, K. Sakamaki, H. Shirakawa, M. Kyotani, *Sciences* **1998**, *282*, 1683; e) L. Zheng, R. C. Urian, Y. Liu, A. K. Y. Jen, L. Pu, *Chem. Mater.* **2000**, *12*, 13; f) V. Pugh, Q. S. Hu, L. Pu, *Angew. Chem.* **2000**, *112*, 3784; *Angew. Chem. Int. Ed.* **2000**, *39*, 3638; g) L. Z. Gong, Q. S. Hu, L. Pu, *J. Org. Chem.* **2001**, *66*, 2358; h) J. Lin, Q. S. Hu, M. H. Xu, L. Pu, *J. Am. Chem. Soc.* **2002**, *124*, 2088; i) Y. Cui, O. R. Evans, H. L. Ngo, P. S. White, W. B. Lin, *Angew. Chem.* **2002**, *114*, 1207; *Angew. Chem. Int. Ed.* **2002**, *41*, 1159.

[3] For resolution of binaphthols, see a) B. Feringa, H. Wynberg, *Bioorg. Chem.* **1978**, *7*, 397; b) F. Toda, K. Tanaka, *J. Org. Chem.* **1988**, *53*, 3607; c) S. Miyano, K. Kawahara, Y. Inoue, H. Hashimoto, *Tetrahedron Lett.* **1987**, *28*, 355; d) W. H. Pirkle, J. L. Schreiner, *J. Org. Chem.* **1981**, *46*, 4988; e) Q. S. Hu, D. Vitharana, L. Pu, *Tetrahedron: Aymmetry* **1995**, *6*, 2123; f) D. Cai, D. L. Hughes, T. R. Verhoeven, P. J. Reider, *Tetrahedron Lett.* **1995**, *36*, 7991; for nonoxidative syntheses of chiral binaphthyl, see g) T. Hayashi, K. Hayashizaki, T. Kiyoi, Y. Ito, *J. Am. Chem. Soc.* **1988**, *110*, 8153; h) M. Shindo, K. Koga, K. Tomioka, *J. Am. Chem. Soc.* **1992**, *114*, 8732; i) A. N. Cammidge, K. V. L. Crepy, *Chem. Commun.* **2000**, 1723; k) J. Yin, S. L. Buchwald, *J. Am. Chem. Soc.* **2000**, *122*, 12051.

[4] a) M. Nakajima, I. Miyoshi, K. Kanayama, S.-I. Hashimoto, *J. Org. Chem.* **1999**, *64*, 2264; b) X. Lin, J. Yang, M. C. Kozlowski, *Org. Lett.* **2001**, *3*, 1137, and references therein.

[5] R. Irie, K. Masutani, T. Katsuki, *Synlett* **2000**, 1433.

[6] a) C. Y. Chu, D. R. Hwang, S. K. Wang, B. J. Uang, *Chem. Commun.* **2001**, 980; b) S. W. Hon, C. H. Li, J. H. Kuo, N. B. Barhate, Y. H. Liu, Y. Wang, C. T. Chen, *Org. Lett.* **2001**, *3*, 869.

[7] Z. Luo, Q. Liu, L. Gong, X. Cui, A. Mi, Y. Jiang, *Chem. Commun.* **2002**, 914.

[8] H. C. Zhang, W. S. Huang, L. Pu, *J. Org. Chem.* **2001**, *66*, 481.

[9] For applications of a similar strategy in other reactions, see a) K. Mikami, T. Korenaga, M. Terada, T. Ohkuma, T. Pham, R. Noyori, *Angew. Chem.* **1999**, *111*, 517; *Angew. Chem. Int. Ed.* **1999**, *38*, 495; b) T. Ooi, Y. Uemastu, M. Kameda, K. Maruoka, *Angew. Chem.* **2002**, *114*, 1621; *Angew. Chem. Int. Ed.* **2002**, *41*, 1551; c) K. Mikami, K. Aikawa, Y. Yusa, *Org. Lett.* **2002**, *4*, 95.

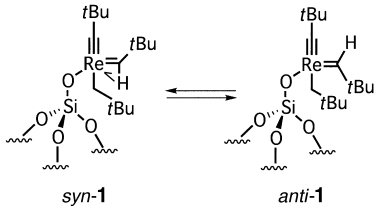
[10] a) L. J. Theriot, G. O. Carlisle, H. J. Hu, *J. Inorg. Nucl. Chem.* **1969**, *31*, 2841; b) J. J. R. Frausto da Silva, R. Wootton, R. D. Gillard, *J. Chem. Soc. A* **1970**, 3369.

Observation of a H-Agostic Bond in a Highly Active Rhenium–Alkylidene Olefin Metathesis Heterogeneous Catalyst by Two-Dimensional Solid-State NMR Spectroscopy**

Anne Lesage, Lyndon Emsley,* Mathieu Chabanas, Christophe Copéret,* and Jean-Marie Basset*

Heterogeneous catalysis is still the industrial cornerstone in the production of basic chemicals, polymers, and in some instances fine chemicals. One of the key problems in developing new heterogeneous catalysts has been the low content of active sites coupled with their diversity, which makes their characterization very difficult and which often does not allow a rational understanding of their reactivity and selectivity. Even in cases where, using approaches such as surface organometallic chemistry (SOMC), well-defined complexes are prepared, a detailed structural characterization of the geometry of such surface species is extremely difficult.

In molecular chemistry the local geometries can be probed by NMR spectroscopy, for example, by measuring scalar coupling constants. So far coupling constants on surfaces could not be determined. Herein we demonstrate how $J_{C,H}$ coupling constants can be measured in solids by using two-dimensional (2D) *J*-resolved spectroscopic methods, and how they are related to the local structure of the well-defined silica-supported rhenium complex **1**. This complex was shown



to be a highly active heterogeneous catalyst for the metathesis of a variety of olefins at room temperature.[1] In addition, two isomers can be obtained upon thermal or photochemical treatment (referred to as *syn* and *anti*, depending on the position of the *t*Bu fragment on the carbene ligand relative to the metallocarbyne), which were both characterized by solid-

[*] Prof. L. Emsley, Dr. A. Lesage
Laboratoire de Stéréochimie et des Interactions Moléculaires (UMR-5532 CNRS/ENS), Laboratoire de Recherche Conventionné du CEA (23 V)
Ecole Normale Supérieure de Lyon
46 Allée d'Italie, 69364 Lyon (France)
Fax: (+33) 4-7272-8384
E-mail: lyndon.emsley@ens-lyon.fr
Dr. C. Copéret, Prof. J.-M. Basset, Dr. M. Chabanas
Laboratoire de Chimie Organométallique de Surface (UMR-9986 CNRS/CPE Lyon)
Ecole Supérieure de Chimie Physique Electronique de Lyon
43, Bd du 11 Novembre 1918, 69616 Villeurbanne Cedex (France)
Fax: (+33) 4-7243-1795
E-mail: coperet@cpe.fr
basset@cpe.fr

[**] We thank the C.N.R.S., the ESCPE-Lyon, and ENS-Lyon for financial support. M.C. is grateful to the French Ministry for Education and Research for a fellowship (MENRT).

  0044-8249/02/4123-4535 $ 20.00+.50/0