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.

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

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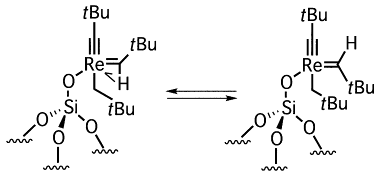
Heterogeneous catalysis is still the industrial cornerstone in the production of basic chemicals, polymers, and in some instances fine chemicals. One of the key problems in developing new heterogeneous catalysts has been the low content of active sites coupled with their diversity, which makes their 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 $J_{\mathrm{C,H}}$ 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-



syn-**1**   *anti*-**1**

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state NMR spectroscopy using short- and long-range two-dimensional carbon–proton through-space correlation experiments.[2] Access to the precise molecular structure of these two metallocarbenes would help in better understanding the high activity of the rhenium complex.

In solution-state NMR studies, heteronuclear *J*-resolved 2D NMR spectroscopy is one of the most basic techniques available to investigate heteronuclear multiplet structures and can be used to measure $J_{C,H}$ couplings with high accuracy.[3] For solid materials, in contrast, the measurement of $J_{C,H}$ couplings is a challenging problem since the size of the scalar interactions is usually much smaller than that of the anisotropic interactions, that is, the dipolar couplings or the chemical shift anisotropies. Thus, in solid-state NMR spectroscopy, heteronuclear *J*-resolved experiments have been limited so far to compounds with fast molecular reorientation,[4] or to mobile organic products intercalated in zeolite channels[5] or kaolinite.[6] As a result of remarkable improvements in the efficiency of homonuclear dipolar decoupling pulse sequences, we have shown that the anisotropic interactions can be suppressed efficiently enough to resolve the heteronuclear $J_{C,H}$ couplings on much more strongly coupled systems under conditions of relatively fast magic angle spinning (MAS).[7,8] Thus a *J*-resolved technique should be applicable to rigid solids, and could be used to measure heteronuclear scalar couplings in strongly coupled systems.

The pulse sequence for the solid-state *J*-resolved experiment that we used in this study is indicated in Figure 1. A cross polarization step first transfers the proton magnetization to the carbon nuclei. During the evolution period t_1, the proton–proton dipolar couplings are removed by the homonuclear decoupling sequence, whereas the remaining inhomogenous interactions, that is, the chemical shift and the heteronuclear couplings, are averaged out by magic angle spinning to their isotropic part, leaving only the isotropic chemical shift and the heteronuclear scalar couplings. As the 180° carbon pulse applied in the middle of t_1 refocuses the chemical shift, the carbon magnetization will be only modulated during t_1 by the heteronuclear $J_{C,H}$ couplings. A *z*-filter is then applied to allow phase sensitive detection in t_1 before direct signal detection in t_2. A two-dimensional Fourier transform yields correlations between heteronuclear *J* multiplet structures (in ω_1) and carbon chemical shifts (in ω_2). Due to the homonuclear decoupling sequence, the heteronuclear couplings extracted in the ω_1 dimension are scaled by a factor λ which can be determined experimentally (see Experimental Section). It is important to underline the fact that the carbon π pulse applied in the middle of the t_1 evolution period refocuses the carbon chemical shift distribution which is often one of the main sources of carbon line broadening in solid species.[9]

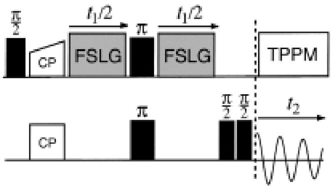

Figure 1. Pulse sequence for the solid-state *J*-resolved experiment (the pulse program and the phase cycle are available from our website[14]). Quadrature detection in ω_1 was achieved by using the TPPI method[15] by incrementing the phase of the first 90° carbon pulse. Proton–proton homonuclear decoupling was performed by using the frequency-switched Lee–Goldburg (FSLG) decoupling sequence,[16] but other homonuclear decoupling schemes can be employed.[8,17] During the acquisition period, TPPM heteronuclear decoupling[18] is applied.

Figure 2 shows the *J*-resolved spectrum recorded on the surface complex (**1**) prepared with ^{13}C labeling at the α positions. The traces extracted along the ω_1 dimension are shown in Figure 3 for various carbon resonance signals. As expected, the CH_3 groups yield a quartet, while the CH_2 and CH groups are correlated in the ω_1 dimension with triplet and doublet structures, respectively. The carbyne resonance of the *syn* rotamer is not split, as this carbon atom is not directly bonded to any proton. $^1J_{C,H}$ coupling constants of 126 Hz are measured for both the CH_3 and CH_2 groups. This is a typical value for H-bearing sp^3 hydridized carbon atoms.

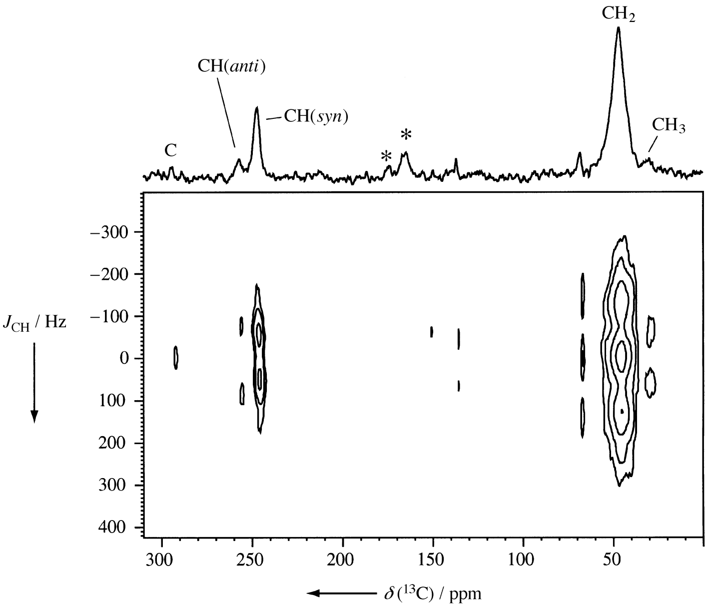

Figure 2. Contour plot of a two-dimensional *J*-resolved spectrum of the surface complex **1**, isotopically enriched in ^{13}C at the α positions, and, at the top, the one-dimensional CP-MAS carbon spectrum (256 scans). The CH_3 resonance signal is weak because the CH_3 groups are unlabeled. The stars indicate spinning sidebands. The other unlabeled peaks correspond to impurities (4% integration by ^{13}C NMR spectroscopy) that arise during the isomerization step carried out at 120°C under argon. The carbyne resonance signal of the *anti* conformer does not appear in this spectrum and in the 2D map because of its low intensity. For further details see the Experimental Section.

The scalar couplings of the metallocarbene CH groups are significantly different for the *syn* and *anti* rotamers (109 and 159 Hz, respectively). This is in agreement with several observations for homogeneous molecular organometallic complexes where *syn* rotamers of alkylidene complexes always have smaller $^1J_{C,H}$ values than the *anti* rotamers.[10] The difference in scalar coupling suggests a difference in bond order of the carbenic C–H bond, stemming from the formation of a three-center, two-electron C-H-Re bond in the *syn* rotamer, which is also referred to as an agostic

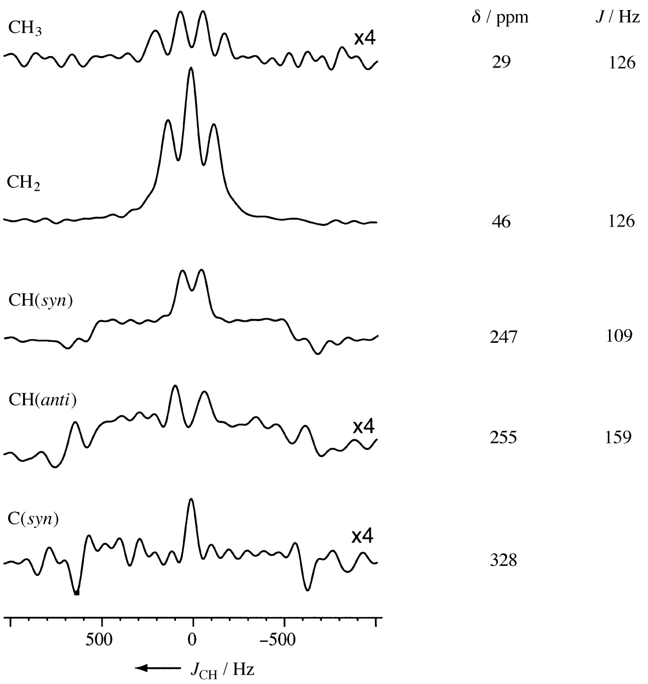

Figure 3. Traces extracted along the ω_1 dimension of the 2D J-resolved spectrum of Figure 2 at different carbon chemical shift frequencies. No signal apodization was applied. The values for the one-bond $J_{C,H}$ couplings were determined by peak deconvolution using Gaussian lineshapes. Errors in the measurement of the scalar couplings are about ± 4 Hz.

interaction.[11] The $^1J_{C,H}$ couplings have indeed been shown to be directly correlated to the degree of agosticity as the coupling varies from its unperturbed value of about 150 Hz to as low as 70 Hz in the most strongly agostic complexes.[12] This variation is logical since an increasing agostic interaction of the proton with the metal center will consequently weaken the C–H bond, which leads to a smaller $^1J_{C,H}$ coupling constant. A relation was established by using the observed change of the M-C-C bond angle from its normal value (120° for a sp^2 carbon) to around 170° for strongly agostic complexes in a range of model alkylidene complexes in solution.[12] The $^1J_{C,H}$ coupling constant can therefore be used to determine the local structure of the alkylidene ligand in the surface complexes. Using this relationship, values of 155 and 120° were obtained for the M-C-C bond angles of the *syn* and *anti* rotamer, respectively. The large value for the M-C-C bond angle for the *syn* rotamer indicates a small M-C-H bond angle of around 100° as a result of the interaction of the C–H bond and the Re center. Formally, complex **1** is a d^0 14-electron complex, assuming that the siloxy ligand is a poor π-donor ligand.[13] The lack of electron density on the metal center is therefore compensated by the participation of the two electrons from the C–H bond in a C–H agostic interaction to the metal. As a result, the formally empty orbital is not available to coordinate an incoming olefin. This is probably the reason for the lower activity of *syn* isomers in the metathesis reaction in solution, and the same situation is likely on the surface, on which it is also possible to control the alkylidene stereochemistry through thermal or photochemical treatment.[2]

Moreover, our data clearly show that the Re center is highly electron deficient, which probably explains the unprecedentedly high activity in olefin metathesis for silica-supported catalysts. They also indicate that the absence of activity of the silica-supported catalysts in classical heterogeneous catalysis is not due to the support per se, but suggest that the rate-determining step is the formation of the propagating center, an alkylidene.

In conclusion, 2D J-resolved solid-state NMR spectrsocopy has allowed us to determine the local structure of a heterogeneous catalyst, and to provide direct experimental evidence for the presence of a H-agostic bond. Note that the only obvious alternative to this method would be to precisely locate the position of the hydrogen atom by X-ray diffraction techniques. The determination of proton positions by this technique is notoriously difficult in the best of cases, and it currently seems unrealistic for surface species using EXAFS-based methods. The method proposed herein provides a unique structural probe of surface species that will yield valuable new insights into the molecular understanding of the active sites in heterogeneous catalysts.

Experimental Section

The NMR experiments were performed on a Bruker DSX 500 spectrometer with a conventional double-resonance 4 mm CP-MAS probe. The sample volume was restricted to the center of the rotor. A total of 48 t_1 increments of 465.5 μs with 4096 scans each were collected. A spectral width of 1073 Hz (uncorrected value) was used in the ω_1 dimension. The rotor spinning frequency was 12 kHz. The proton radio frequency (RF) field strength was set to 83 kHz during t_1 (FSLG decoupling) and during acquisition (TPPM decoupling). The lengths of carbon and proton 180° pulses were 6.5 and 6 μs, respectively. For the cross-polarization (CP) step, the RF field was set to 62 kHz for carbon, while a ramped RF field was applied on protons and matched to obtain optimal signals. The contact time for CP was 1 ms and the recycle delay was 2 s. The sample temperature was set to 20 °C. The overall experimental time was 110 h.

Details to Figure 2: Approximately 20 mg of sample was used. The surface area in these samples was around 200 m^{2}g^{-1}. The one-dimensional CP-MAS spectrum was assigned by one- and two-dimensional heteronuclear correlation spectroscopy as reported in reference [2]. The experimental scaling factor λ of the FSLG decoupling sequence was obtained by comparing the proton spectra of L-alanine recorded under fast MAS conditions (30 kHz) and under FSLG decoupling, as described in reference [19]. At a RF field of 83 kHz, a scaling factor of 0.52 was found, which gave a corrected spectral width of 2065 Hz in the ω_1 dimension. Note that the pulse sequence used in this study differs from those proposed so far for solid-state studies: the J-resolved experiments used previously to obtain 2D J spectra in highly mobile solids were based on the gated decoupler method, which reduces the scaling factor of the homonuclear decoupling sequence by an additional factor of one half. Notably, the gated decoupler technique is not suitable for strongly coupled systems, and in our case it would not have allowed a clear identification of the agostic bond. Note that although the surface complex is not entirely rigid, since motion is allowed around the Si–O bond, homonuclear decoupling during t_1 is necessary for the $J_{C,H}$ couplings to be resolved.

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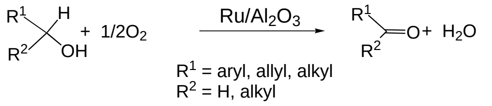
Supported Ruthenium Catalyst for the Heterogeneous Oxidation of Alcohols with Molecular Oxygen**

Kazuya Yamaguchi and Noritaka Mizuno*

Although catalytic oxidation of alcohols to carbonyl compounds has attracted much attention both in industrial processes and in organic syntheses,[1–3] alcohols are traditionally oxidized by non-catalytic methods with stoichiometric oxidants such as dichromate and permanganate.[1–3] These methods produce enormous amounts of metal salts as wastes. Much effort has been made to develop homogeneous catalytic systems to solve these problems.[4–6] However, most systems are applicable only for the oxidation of activated benzylic and allylic alcohols, or large quantities of additives such as NaOAc, NaOH, and K_2CO_3 are needed.[7–10] There is little known about the oxidation of alcohols with molecular oxygen, which could be applied to a wide range of alcohols. If these oxidation reactions could be performed by using solid-supported catalysts (heterogeneous catalysis), they would be considerably cheaper and environmentally more friendly because of the ease with which the catalysts could be separated from products and recycled.[11–14] Examples of solid-supported catalysts that have been tested include tetrapropylammonium perruthenate (TPAP)/MCM-41,[15] Ru/CeO_2,[16] Ru-hydrotalcite,[17] Ru-hydroxyapatite,[18] $[RuCl_2(p\text{-cymene})]_2$/activated carbon,[19] Pd-hydrotalcite,[20] and Pd or Pt on activated carbon.[21] However, heterogeneous oxidation reactions are limited to activated alcohols and/or have turn over numbers (TONs) which are very low (less than 20).[15–21] If oxidation reactions could be carried out without solvents, then the system would facilitate the separation of catalyst from products. Despite the advantage of using solid catalysts without solvents or additives for oxidation of both activated and non-activated alcohols, nothing has been reported on the use of highly active solvent-free heterogeneous catalysts with only molecular oxygen. Herein we report an effective aerobic heterogeneous oxidation reaction of both activated and non-activated alcohols, which may have a sulfur atom, a nitrogen atom, or a carbon-carbon double bond, by using molecular oxygen or air catalyzed by Ru supported on alumina (Ru/Al_2O_3) and demonstrate the use of solvent-free oxidation reactions [Eq. (1)]. The results we present offer a strategy for the design of heterogeneous alcohol-oxidation catalysts for use in conjunction with molecular oxygen.



(1)

The Ru/Al_2O_3 system had high catalytic activities for the oxidation of activated and non-activated alcohols with only 1 atm of O_2 as shown in Table 1. Reaction selectivity was over 97% in all cases and all primary and secondary benzylic alcohols were converted quantitatively into the corresponding benzaldehydes and ketones, respectively. Primary and secondary allylic alcohols afforded the corresponding enals or enones without intramolecular hydrogen transfer or geometrical isomerization of the double bonds. Additionally, the catalytic system efficiently oxidized non-activated alcohols to the corresponding carbonyl compounds: for the oxidation of 2-octanol, 2-octanone was produced in a 91% yield (entry 14). Similarly, alicyclic alcohols such as cyclopentanol and cyclooctanol were selectively oxidized to the corresponding cyclic ketones (entries 15 and 16). Less reactive aliphatic primary alcohols, 1-octanol and 1-decanol, were also oxidized. However, increasing the reaction time did not improve the yields of the aldehydes because of successive oxidation to the corresponding carboxylic acids. The addition of a small amount of hydroquinone (1 equiv based on Ru) completely

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