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Better Characterization of Surface Organometallic Catalysts through Resolution Enhancement in Proton Solid State NMR Spectra

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Delayed-acquisition methods, namely, echo and constant-time-acquisition approaches, allow a significant improvement in resolution in the proton solid state NMR spectra of surface organometallic catalysts such as [*syn*-(SiO)Mo(=NAr)(=CH^{t}Bu)(CH$_2$^{t}Bu)] and [(≡SiO)Re(≡C^{t}Bu)(=CH^{t}Bu)(CH$_2$^{t}Bu)] (*syn*/*anti* ratio = 1:1). This enables the observation of all of the proton resonances, which is not possible with the simple proton single-pulse technique under magic-angle spinning. For example, the methylene protons of the neopentyl ligands, buried in the large peak associated with all of the methyls in the ^{1}H MAS spectrum, can easily be identified by recording a delayed-acquisition spectrum (resolution enhancement of a factor of 3 is obtained). Moreover, combining constant-time acquisition with heteronuclear carbon–proton correlation spectroscopy also improves the resolution of the 2D HETCOR spectra.

Introduction

Proton NMR spectroscopy is an extensively used tool for structure determination of molecules in solution. In liquids, highly resolved proton spectra are obtained because of fast molecular tumbling, which, in most cases, fully average out the anisotropic interactions. In contrast, the proton spectra of solid compounds are usually dominated by the strong dipole−dipole couplings present among the dense network of proton spins. This results in unresolved spectra containing very broad resonances (typically 40 kHz in a static sample). For complex molecular systems, the rotation of the sample alone around the magic angle ($\theta_m = 54.7°$) is usually insufficient to fully average these anisotropic interactions and retrieve any chemical shift information.

Several methods have been proposed to remove the ^{1}H−^{1}H homonuclear dipolar interactions in a more efficient way, such as very fast magic-angle spinning (MAS),[1] dilution by deuterium,[2,3] and CRAMPS (combined rotation and multiple-pulse sequences) techniques, which combine the rotation of the sample at the magic angle with the application of a homonuclear decoupling sequence.[4] With the recent development of new, efficient proton−proton decoupling schemes such as PMLG,[5−9] DUMBO,[10,11] and eDUMBO,[12] the CRAMPS approach has been shown to lead to a resolution

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of less than 0.2 ppm in model powdered compounds. Despite the introduction of these sophisticated techniques, dipolar broadening still seriously limits the resolution of proton spectra of solid molecules and, therefore, the use of proton NMR spectroscopy as a routine technique for the structural characterization of medium-sized molecules in solids.

In this article, we investigate the resolution of proton NMR spectra of well-defined single-site surface organometallic compounds supported on silica. These surface complexes constitute an important class of heterogeneous catalysts, designed and synthesized following a molecular approach (called surface organometallic chemistry).[13,14] We have recently shown that one- and two-dimensional solid state NMR spectroscopy can be used to characterize in detail the structure of these surface complexes.[15,16]

The challenging question of how to obtain higher-resolution proton NMR spectra is posed in a relatively different way for molecules grafted onto a surface as compared to ordinary molecular solids. Indeed, for molecules on surfaces, magic-angle spinning alone at moderate frequencies (10 kHz) is usually sufficient to obtain fairly well-resolved proton spectra. This is because (i) these compounds, although covalently linked to the surface, still have several degrees of motional freedom that partially average out the dipolar interactions (such as rotation about the oxygen−metal bond in the case of a mono-grafted species) and (ii) single-site catalysts are usually dispersed on the surface, typically separated by more than 10 Å, which significantly reduces the proton density at a given site. Proton line widths of 1 ppm are typically observed under MAS conditions. The observed residual broadening is assigned to both chemical shift distributions (corresponding to a continuum of very slightly different molecular structures over the surface) and residual anisotropic interactions.

We have recently shown for [*syn*-(SiO)Mo(═NAr)(═CH^{t}Bu)(CH$_2$^{t}Bu)] (**1**)[17] (Ar = 2,6-di-isopropylphenyl) that a slight, but significant, improvement in proton resolution can be observed by applying DUMBO homonuclear decoupling during the acquisition of the proton spectrum, the line width of the CH$_2$ proton being thus reduced from 390 to 260 Hz. In this article, we investigate an alternative "high-resolution" approach to the proton spectroscopy of surface catalysts, namely constant-time (CT) acquisition of proton spectra. This approach has been previously shown by us to provide a significant improvement in the resolution of ^{1}H spectra of powdered rigid solids.[18] For the Mo-based catalyst precursor **1**, we show that dramatic enhancement in resolution, up to a factor 3, is observed when the proton spectrum is acquired over a constant-time period. A comparison with delayed acquisition is provided. Although, as reported for powdered solids, this approach suffers from relatively poor sensitivity, we show that a constant-time carbon−proton correlation experiment is feasible on this type of compound and provides a significant gain in resolution compared to standard heteronuclear correlation spectroscopy (HETCOR). The enhancement in proton resolution using constant-time acquisition is finally investigated for a Re-based catalyst precursor [(≡SiO)Re(≡C^{t}Bu)(═CH^{t}Bu)(CH$_2$^{t}Bu)] (**2**)[16,19] (*syn*/*anti* ratio = 1:1) to illustrate the generality of the approach. In both cases **1** and **2**, this approach allows for the identification of more resonances than does the conventional method.

Results and Discussion

Figure 1 shows a comparison between the (a) single-pulse, (b) delayed-acquisition, and (c) constant-time-acquisition MAS proton spectra of complex **1**. The single-pulse spectrum (Figure 1a) consists of four well-resolved resonances, assigned to the following protons: *syn*-[Mo](═C*H*^{t}Bu) (H$_3$, 11.7 ppm), Ar*H* (H$_5$, 6.8 ppm), C*H* (^{i}Pr) (H$_4$, 3.5 ppm) and C*H*$_3$ (H$_1$;H$_1{}'$;H$_1{}''$, 0.9 ppm), as described recently.[17] The one-dimensional (1D) delayed-acquisition spectrum of (**1**) (Figure 1b) was recorded using the pulse sequence shown in Figure 2a. The delayed-acquisition experiment, which was first proposed in the mid-1990s as an alternative approach for observing narrow proton line widths in solid samples,[20−24] consists of a 90° proton pulse followed by a spin−echo period before direct acquisition of the NMR signal. In the resulting spectrum, the intensities of the proton resonances are attenuated through the transverse dephasing of coherences during the spin−echo period, the signal attenuation being dependent on the magnitude of the so-called refocused transverse coherence lifetime, T_2',[25−27] of the proton spins.

As described in previous reports, T_2' corresponds to the time constant characterizing the decay of the proton signal intensity, as observed in a spin−echo experiment. The π pulse applied in the middle of the echo period refocuses some interactions, such as the chemical shift distributions or the refocusable terms of the residual dipolar coupling interactions, but some residual dipolar terms remain unrefocusable. Thus, T_2' can be much longer than the apparent transverse dephasing time T_2^*, which is the inverse of the apparent line width Δ^* measured in the single-pulse 1D spectrum, i.e.,

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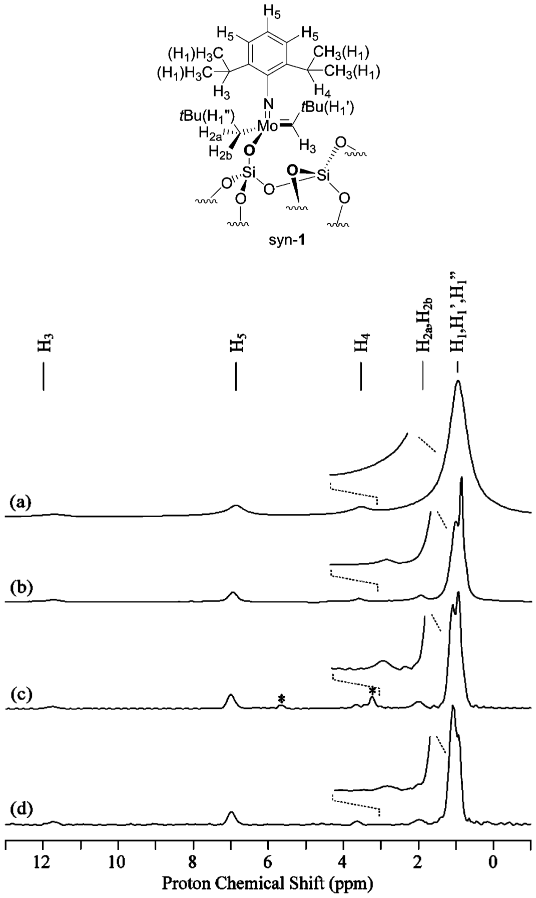

Figure 1. Molecular structure and one-dimensional proton MAS spectra of $[syn\text{-}(\equiv SiO)Mo(=NAr)(=CH^{t}Bu)(CH_2{}^{t}Bu)]$ (**1**)[17] (a) Single-pulse spectrum (8 scans). (b) Delayed-acquisition spectrum (32 scans) acquired using the pulse sequence of Figure 2a with an echo period 2τ of 10 ms. (c) Constant-time proton spectrum. This spectrum was constructed from a 2D spectrum (acquired using the pulse sequence of Figure 2b and shown in Figure S1) by summing ω_1 traces extracted along ω_2 at the relevant proton frequencies (see text for details). The constant time T was set to 10 ms. A total of 196 t_1 points with 8 scans each were collected. Asterisks indicate small artifacts present in the 2D spectrum. (d) Constant-time proton spectrum of **1** obtained by grafting $[Mo(=NAr)(=CH^{t}Bu)(CH_2{}^{t}Bu)_2]$ onto deuterated silica. The experimental conditions were the same as in c. Insets above the spectra show expanded details between 1 and 3 ppm.

$T_2{}^* = 1/\pi\Delta^*$.[12] In the delayed-acquisition experiment, an enhancement in the resolution of proton spectra is mostly expected for the following reasons. The observed spectrum is, in fact, the sum of spectra resulting from each surface molecule. These molecules can vary very slightly in chemical shift as a result of variations in the local environment (silica is amorphous).[28] This produces a spectral broadening due to chemical shift. The molecules are all different because they are oriented in the powder in random directions. The dipolar broadening, which is the primary source of T_2', depends on orientation, and so, it is expected to vary somewhat from one molecule to another. Also dipolar interactions depend on local proton density and vary from one chemical group to another.

Thus, we expect two effects in the delayed-acquisition spectrum. First, during the τ delay, protons in molecules oriented so as to yield shorter T_2' will decay more than those oriented so as to yield long T_2'. Therefore, the delayed spectrum will be dominated by the molecules with long T_2' and thus smaller dipolar interactions. This will lead to narrower lines and, therefore, increased in resolution. Second, we expect intensity variations from site to site, reflecting the longer T_2' values expected for mobile methyl groups, for example, as compared to rigid methylene groups. Both of these effects are apparent in Figure 1b, where we first remark that the most intense resonance, which is labeled H_1, H_1', and H_1'' and corresponds to the methyl protons, is now clearly split into two components at 1.0 (H_1) and 0.8 (H_1' and H_1'') ppm. The resonance at 1.0 ppm can be assigned to the methyl protons of the di-isopropylphenylimido moiety, whereas that at 0.8 ppm likely corresponds to the methyl protons of both the neopentyl $[Mo](CH_2C(CH_3)_3)$ and neopentylidene $[Mo](=CHC(CH_3)_3)$ ligands, in agreement with previous works on similar molecular systems.[29−31] An additional weak resonance (H_2), which was not observed in the single-pulse spectrum of Figure 1a, is now clearly visible at 2.0 ppm. It might correspond to either methylene protons $[Mo](CH_2{}^{t}Bu)$ or to (unreacted) silanols present on the surface[32,33] (see below).

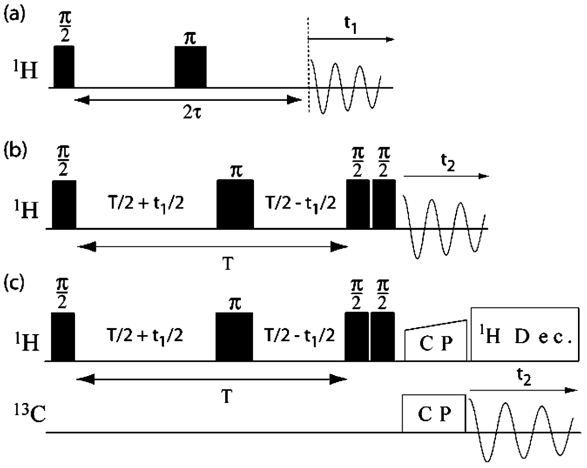

Figure 2. Pulse sequences used for (a) the 1D delayed-acquisition experiment, (b) the 2D constant-time experiment, and (c) the 2D heteronuclear constant-time experiment. In b and c, quadrature detection in ω_1 was achieved using the States method[36] by incrementing the phase of the second 90° proton pulse. The pulse programs are available from our web site[37] or upon request to the authors.

As mentioned above, the resolution enhancement observed in the methyl region is likely due to differences in transverse refocused coherence lifetimes T_2', combined with the selection of molecules with long T_2' species. Table 1 reports, for the five distinct proton resonances of **1**, the characteristic refocused and apparent transverse dephasing times (T_2' and $T_2{}^*$). The decays of proton magnetization as a function of

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Table 1. Proton Chemical Shifts and Corresponding Assignments for the Surface Complexes [*syn*-(≡SiO)Mo(═NAr)(═CH^{t}Bu)(CH$_2$^{t}Bu)] (**1**)[17] and [(≡SiO)Re(≡C^{t}Bu)(═CH^{t}Bu)(CH$_2$^{t}Bu)] (**2**)[16] (*syn*/*anti* Ratio = 1:1)[a]

site	assignment	^{1}H chemical shift (ppm)	T_2*[b] (ms)	T_{2a}[c] (ms)	T_{2b}[c] (ms)
	[*syn*-(≡SiO)Mo(═NAr)(═CH^{t}Bu)(CH$_2$^{t}Bu)] (**1**)				
H_1, H_1'	C*H*$_3$ (^{t}Bu)	0.8	1.4[d]	5.3[e]	0.9[e]
H_1	C*H*$_3$ (^{i}Pr)	1.0	1.4[d]	5.1[e]	1.1[e]
H_{2a}, H_{2b}	[Mo]─C*H*$_2$^{t}Bu	2.0	–[f]	5.6	1.1
H_4	C*H* (^{i}Pr)	3.5	3.4	3.6	0.5
H_5	Ar*H*	6.8	1.4	4.9	0.5
H_3	*syn*-[Mo]═C*H*^{t}Bu	11.7	1.7	4.7	0.9
	[(≡SiO)Re(≡C^{t}Bu)(═CH^{t}Bu)(CH$_2$^{t}Bu)] (**2**) (*syn*/*anti* Ratio 1:1)				
H_1	C*H*$_3$ (C^{t}Bu)	1.1	3.5	5.8	
H_1'	C*H*$_3$ (CH^{t}Bu)	1.2	2.9	3.6	
H_1''	C*H*$_3$ (CH$_2$^{t}Bu)	1.4	2.7	3.9	
$H_{2a,anti}$	*anti*-[Re]─C*H*$_2$^{t}Bu	2.0	–[f]	4.3	
$H_{2a,syn}$	*syn*-[Re]─C*H*$_2$^{t}Bu	2.6	2.6	3.6	
$H_{2b,syn}$	*syn*-[Re]─C*H*$_2$^{t}Bu	3.0	2.0	4.1	
$H_{2b,anti}$	*anti*-[Re]─C*H*$_2$^{t}Bu	3.1	–[f]	3.7	
$H_{3,syn}$	*syn*-[Re]═C*H*^{t}Bu	11.0	1.3	6.4	
$H_{3,anti}$	*anti*-[Re]═C*H*^{t}Bu	12.6	1.9	6.6	

[a] For each resonance, the T_2* value, calculated from the measured proton line width at half-height, is indicated, together with fitted values of the refocused dephasing time T_2' as measured from spin–echo experiments. [b] T_2* values were calculated as $1/\pi\Delta^*$, where Δ^* is the apparent line width at half-height that is measured in an ^{1}H single-pulse spectrum. [c] Transverse dephasing times T_2' were obtained by fitting the intensity of the proton resonances measured in a spin–echo experiment as a function of the echo length τ using the biexponential function $p\ \exp(-2\tau/T_{2a}') + (1 - p)\ \exp(-2\tau/T_{2b}')$ for **1** and the monoexponential function $q\ \exp(-2\tau/T_2')$ for **2**. [d] Common values due to overlapping resonances (see Figure 1a). [e] Different values due to resolution gain (see Figures 1b–d and S1). [f] Unresolved resonance in the ^{1}H single-pulse spectrum (see Figures 1a and 4a).

the spin–echo length (observed using the pulse sequence of Figure 2a with varying delays τ) could be properly fitted with a biexponential function and two characteristic times T_{2a}' and T_{2b}' (as already observed for some other solid species[34]). Although relatively small, differences in T_2' are observed among the various resonances. More importantly, we remark that T_{2a}' (the longer refocused time constant) and T_2* differ by a factor ranging between 2 and 3.8. Thus, for resonance H_4, for instance, the refocused line width corresponding to the measured T_{2a}' value (and calculated as $1/\pi T_{2a}'$) is 65 Hz, whereas the apparent line width in the single-pulse proton spectrum is 227 Hz. In delayed acquisition, long T_2' values are favored, but the effect of T_2' broadening is not removed.

Proton resonances that are entirely free of the nonrefocusable broadening due to T_2' (65 Hz in the previous example) and that contain only the refocusable terms (notably chemical shift) can, in principle, be observed by applying a constant-time acquisition of the ^{1}H signal.[18] Figure 2b shows the pulse sequence for the constant-time experiment used here. This is a two-dimensional (2D) experiment, in which acquisition of the signal in t_2 starts at a constant time T after the initial 90° proton pulse; a π pulse is shifted from the middle to the end of this constant-time interval progressively from one t_1 increment to another. As already described in detail,[18] the nonrefocusable interactions, which are insensitive to the position of the π pulse, are active during the whole constant time T, whereas during t_1, the evolution of the proton magnetization is modulated only by the refocusable interactions. This yields a 2D spectrum correlating along the diagonal the constant-time spectrum in ω_1 with the normal MAS spectrum in ω_2. The 1D constant-time proton spectrum is simply obtained by summing the ω_1 traces extracted along ω_2 at the various proton frequencies.

The 1D proton constant-time spectrum of **1**, recorded with a T value of 10 ms, is shown in Figure 1c. (Figure S1 in the Supporting Information shows the full 2D spectrum from which this spectrum was extracted.) A constant-time value of 10 ms was found experimentally to be a good compromise between resolution in ω_1 (the maximum value of t_1 cannot exceed T) and sensitivity. The CT proton spectrum shows an additional increase in proton resolution over the delayed-acquisition spectrum (Figure 1b), although they are globally similar. Thus, the H_4 resonance is now 95 Hz broad at half width in the CT spectrum compared to 130 Hz in the delayed-acquisition spectrum. This corresponds to a factor 1.6–2.3 in line width reduction in comparison to the conventional single-pulse spectrum of Figure 1a (214 Hz). In particular, the H_2 resonance at 2 ppm is clearly resolved. Note that we observed experimentally that very fast MAS (up to 30 kHz) does not help to improve the resolution of the single-pulse proton spectra (data not shown).

To obtain an unambiguous assignment of the signal at 2 ppm, which could potentially correspond to either methylene protons or unreacted silanols, a constant-time experiment (T = 10 ms) was conducted on complex **1** obtained by grafting [Mo(═NAr)(═CH^{t}Bu)(CH$_2$^{t}Bu)$_2$] onto deuterated silica instead of protonated silica (i.e., SiO*D* silanols in place of SiO*H* silanols). The corresponding 1D proton spectrum (Figure 1d) is similar to that obtained with protonated silica (Figure 1c), indicating without a doubt that the proton resonance at 2.0 ppm does not correspond to unreacted silanols (in agreement with IR spectroscopy data, which show the consumption of most of the surface silanols, as reported previously).[17] *Note that this unambiguous assignment could not have been drawn from conventional single-pulse spectra, where the methylene resonance is not resolved.*

The resolution enhancement observed in the constant-time experiment occurs at the expense of the signal-to-noise ratio, given that, as reported previously,[18] the proton magnetization is attenuated during the constant time T by the nonrefocusable interactions. (Note that, in principle, the sensitivity of the experiment could potentially be improved slightly by applying homonuclear decoupling during the constant-time period.[18] However, such experiments are significantly more complex to implement and can lead to the presence of spectral artifacts that compromise the potential gain in sensitivity. We are currently investigating ways to implement this experiment in a robust way, and results will be presented elsewhere.) Despite this poor sensitivity, a 2D heteronuclear (HETCOR) constant-time experiment was feasible on complex **1** using the pulse sequence described in Figure 2c. In this experiment, the proton constant-time indirect evolution period was followed by a cross-polarization step, which

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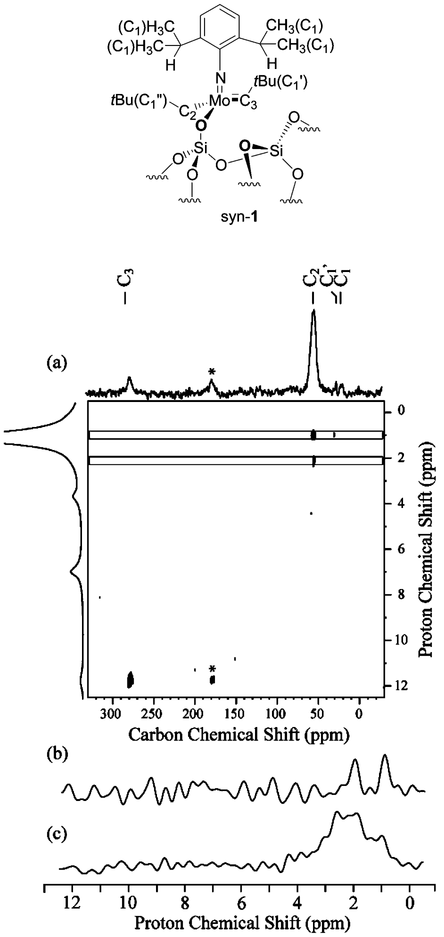

Figure 3. (a) 2D carbon−proton constant-time MAS HETCOR spectrum of **1**. A complex that was fully ^{13}C-enriched at the α positions was used (position C_2 and C_3 as labeled in the molecular structure shown above). The constant time *T* was set to 5 ms, and the contact time for the CP step was 1 ms. The recycle delay was set to 1 s, and the spinning frequency was 10 kHz. A total of 32 t_1 increments with 8192 scans each were collected ($t_{1\max} = 5$ ms) The total acquisition time of the experiment was 110 h. The 1D carbon-13 CP MAS spectrum (256 scans) and the 1D single-pulse proton spectrum (8 scans) are shown above and to the left, respectively, of the 2D spectrum. Asterisks denote spinning sidebands. (b) Proton trace extracted from the 2D spectrum along ω_1 at the methylene carbon C_3 chemical shift (56 ppm). (c) Same trace extracted from a conventional HETCOR spectrum[17] acquired with a total of 96 t_1 increments with 512 scans. The recycle delay was set to 2 s, and the contact time for the CP step 1 ms. The total acquisition time of the experiment was 28 h. The carbon chemical shifts in **1** are as follows: C_1, 22 ppm; C_1' and C_1'', 30 ppm; C_2, 56 ppm; and C_3, 279 ppm, as already reported.[17]

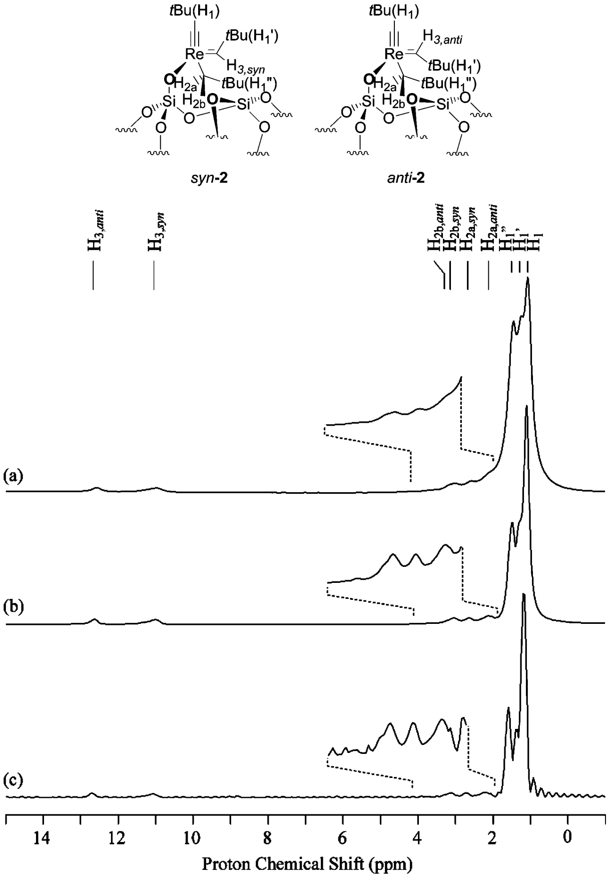

Figure 4. Molecular structure and one-dimensional MAS proton spectra of [(≡SiO)Re(≡C^{t}Bu)(=CH^{t}Bu)(CH$_2$^{t}Bu)] (**2**)[16] (*syn*/*anti* ratio = 1:1). (a) Single-pulse proton spectrum (8 scans). (b) Delayed-acquisition proton spectrum (32 scans) acquired with an echo period 2τ of 10 ms. (c) Constant-time proton spectrum. This spectrum was constructed from a 2D spectrum as detailed in the text. The constant time *T* was set to 10 ms. A total of 196 t_1 points with 8 scans each were collected. Insets above the spectra show expanded details between 1.9 and 4.2 ppm.

allowed the transfer of proton magnetization to the neighboring carbon spins via dipolar through-space interactions. The carbon magnetization was then detected during t_2 under heteronuclear decoupling. After a 2D Fourier transform, correlations were obtained between the high-resolution proton dimension in ω_1 and the carbon spectrum in ω_2. The 2D constant-time HETCOR spectrum of **1** recorded with a *T* value of 5 ms is shown in Figure 3a. In this experiment, for sensitivity reasons, we used a surface complex that was fully carbon-13-labeled at the α positions (carbons C_2 and C_3 in the structure shown above the 2D spectrum). In addition to the correlation at (ω_1, 11.7 ppm; ω_2, 279 ppm) corresponding to the alkylidene moiety [Mo](=*CH*^{t}Bu) C_3, as previously assigned, and to a very weak correlation at (ω_1, 0.8 ppm; ω_2, 31 ppm) corresponding to the methyl C_1' of the neopentyl group, the 2D spectrum shows two correlation peaks in the proton dimension at 0.8 and 2.0 ppm with the methylene carbon [Mo](*CH*$_2$^{t}Bu) C_2 at 56 ppm. They are respectively assigned to an indirect long-range connectivity with the methyl protons of the ^{t}Bu group and to the one-bond correlation with the methylene protons. These two connectivities have about the same intensity, as shown in Figure 3b in the ω_1 trace extracted along ω_2 at the C_3 chemical shift, which can be rationalized by the fact that the methyl protons are likely less attenuated during the constant-time period than the more strongly coupled CH$_2$ protons. Figure 3c shows the same proton trace extracted from a conventional HETCOR spectrum,[17] for which the distinction between the direct and indirect correlations was not clear. The constant-time experiment provides a significant gain in resolution, allowing in this case the unambiguous assignment of the methylene protons at 2 ppm.

Figure 4 shows a comparison between (a) a single-pulse proton spectrum, (b) a delayed-acquisition spectrum, and (c) a constant-time-acquisition proton spectrum recorded on another well-defined organometallic complex grafted on silica, namely, [(≡SiO)Re(≡C^{t}Bu)(=CH^{t}Bu)(CH$_2$^{t}Bu)] (**2**) present on the surface as a mixture of two rotamers, *syn* and *anti*, in a 1:1 ratio. The synthesis and detailed structural characterization of this heterogeneous rhenium alkylidene complex has been recently reported.[16,19] As for the case of the Mo complex **1**, this comparison very clearly demonstrates that constant-time acquisition provides a net improvement in resolution. This is especially true in the aliphatic part of the spectrum, where resonances between 1.9 and 4.2 ppm (see the insets in Figure 4), which are barely visible in the single-pulse proton spectrum (Figure 4a), are clearly observable in the delayed and constant-time experiments (Figure 4b and c). They correspond to the four resonances of the diastereotopic methylene protons in the *syn* and *anti* rotamers and can be potentially assigned by analogy with molecular compounds as follows: *syn*-[Re]($\mathrm{C}H_\mathrm{a}\mathrm{H}_\mathrm{b}{}^t\mathrm{Bu}$) ($\mathrm{H}_{2\mathrm{a,syn}}$, 2.6 ppm), *syn*-[Re]($\mathrm{CH}_\mathrm{a}H_\mathrm{b}{}^t\mathrm{Bu}$) ($\mathrm{H}_{2\mathrm{b,syn}}$, 3.0 ppm), *anti*-[Re]($\mathrm{C}H_\mathrm{a}\mathrm{H}_\mathrm{b}{}^t\mathrm{Bu}$) ($\mathrm{H}_{2\mathrm{a,anti}}$, 2.0 ppm), and *anti*-[Re]($\mathrm{CH}_\mathrm{a}H_\mathrm{b}{}^t\mathrm{Bu}$) ($\mathrm{H}_{2\mathrm{b,anti}}$, 3.1 ppm). [The liquid-state NMR proton spectrum of [POSSORe($\equiv\mathrm{C}^t\mathrm{Bu}$)($=\mathrm{CH}^t\mathrm{Bu}$)($\mathrm{CH}_2{}^t\mathrm{Bu}$)] displays four peaks in the 2−3 ppm area assigned to the *syn*-[Re]($\mathrm{C}H_\mathrm{a}H_\mathrm{b}{}^t\mathrm{Bu}$) ($\delta$ = 2.56 and 3.00 ppm) and *anti*-[Re]($\mathrm{C}H_\mathrm{a}H_\mathrm{b}{}^t\mathrm{Bu}$) ($\delta$ = 2.20 and 3.14 ppm) protons].[16] In the spectra of Figure 4, the two weak resonances at low field correspond to the *syn*-[Re]($=\mathrm{C}H^t\mathrm{Bu}$) ($\mathrm{H}_{3,\mathrm{syn}}$, 11.0 ppm) and *anti*-[Re]($=\mathrm{C}H^t\mathrm{Bu}$) ($\mathrm{H}_{3,\mathrm{anti}}$, 12.6 ppm) protons, whereas the methyl resonances are assigned to the $\mathrm{C}H_3$ [neopentyl, [Re]($\mathrm{CH}_2{}^t\mathrm{Bu}$)] ($\mathrm{H}_1''$, 1.4 ppm), $\mathrm{C}H_3$ [neopentylidene, [Re]($=\mathrm{CH}^t\mathrm{Bu}$)] ($\mathrm{H}_1'$, 1.2 ppm), and $\mathrm{C}H_3$ [neopentylidyne, [Re]($\equiv\mathrm{C}^t\mathrm{Bu}$)] ($\mathrm{H}_1$, 1.1 ppm) groups as reported earlier.[16]

Note that, for the methyl groups, we do see a striking effect of the differences in T_2', discussed above, because of the probably highly mobile methyl group of neopentylidine, which should have a long T_2' value, and the other two methyl groups of neopentylidene and neopentyl, which are probably more rigid and thus have shorter T_2' values. This results in the pattern being observed in Figure 4c.

Conclusion

In conclusion, we have shown that, by using a simple MAS scheme for the constant-time acquisition of the proton signal, a significant improvement in resolution can be observed in the NMR spectra of surface organometallic catalyst precursors. In the complex [*syn*-(SiO)Mo($=$NAr)($=\mathrm{CH}^t\mathrm{Bu}$)($\mathrm{CH}_2{}^t\mathrm{Bu}$)], this approach allowed for the unambiguous observation and assignment of the methylene protons. We believe that the constant-time-acquisition technique, which can be easily implemented on modern spectrometers, might become a routine technique to characterize grafted species, for which the resolution provided by MAS alone is not always sufficient to clearly resolve all the proton resonances. (Note that any new resonance that is possibly observed in a one-dimensional constant-time experiment should be confirmed, for example, by HETCOR.) Despite the fact that the gain in resolution is counterbalanced by a loss in sensitivity, we have shown that the constant-time-acquisition approach can also be applied in heteronuclear carbon−proton correlation spectroscopy, thereby allowing for a complete high-resolution spectral characterization.

Experimental Procedures

General Procedures. Sample Preparation. [*syn*-($\equiv$SiO)Mo($=$NAr)($=\mathrm{CH}^t\mathrm{Bu}$)($\mathrm{CH}_2{}^t\mathrm{Bu}$)] (**1**)[17] and [($\equiv$SiO)Re($\equiv\mathrm{C}^t\mathrm{Bu}$)($=\mathrm{CH}^t\mathrm{Bu}$)($\mathrm{CH}_2{}^t\mathrm{Bu}$)] (**2**)[16,19] (*syn*/*anti* ratio = 1:1) were synthesized as described previously.

Solid State NMR Experiments. All experiments were performed on a Bruker Avance 500 WB spectrometer (proton frequency 500.13 MHz) using a conventional double-resonance 4-mm CP MAS probe. Full rotors were filled in a glovebox and tightly closed. Approximately 20 mg of each sample was used. Chemical shifts are reported in ppm downfield from SiMe_4 referenced at 0.0 ppm. For all experiments, the rotor spinning frequency was 12.5 kHz. For the constant-time HETCOR spectrum, the proton radio-frequency (RF) field was set to 83 kHz for TPPM-15[35] heteronuclear decoupling during acquisition. For the CP step, a ramped RF field centered at 60 kHz was applied on the protons, and the carbon field strength was matched to obtain optimal signal. A 1-ms contact time was used. Unless otherwise specified, the recycle delay was set to 2 s. Other experimental details are given in the figure captions.

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Supporting Information Available: Two-dimensional proton constant-time MAS spectrum of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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