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Perhydrocarbyl Re^{VII} Complexes: Comparison of Molecular and Surface Complexes

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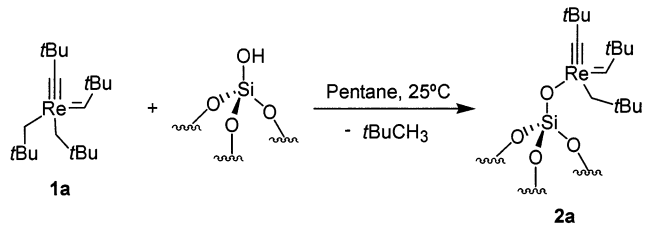
Abstract: The molecular complex [Re(≡C^{t}Bu)(=CH^{t}Bu)(CH$_2$^{t}Bu)$_2$] (**1**) reacts with a silica partially dehydroxylated at 700 °C to give *syn*-**2**, [(≡SiO)Re(≡C^{t}Bu)(=CH^{t}Bu)(CH$_2$^{t}Bu)], as a single isomer according to mass-balance analysis, IR, and solid-state NMR spectroscopy. 1D and 2D solid-state NMR (HETCOR and long-range HETCOR) on a ^{13}C-labeled-**2** has allowed us to observe the chemical shifts of all carbons (including those that are not labeled) and ascertain their assignments. Moreover, EXAFS data are consistent with the presence of two carbons at a relatively short distance (1.79 Å), which cannot be deconvoluted, but which are consistent with the presence of alkylidene and alkylidyne carbons along with two other first neighbors at a longer distance (2.01 Å), the alkyl carbon and the O atom by which the Re is attached to the surface. Moreover, the data also suggest the presence of a siloxane bridge of the silica surface at 2.4 Å in the coordination sphere of the Re center. Thermal and photochemical treatment allow us to observe the anti isomer, which was also fully characterized by 1D and 2D solid-state NMR. This behavior parallels the reactivity of molecular Re complexes, and their respective ^{1}H and ^{13}C chemical shifts match those of the corresponding molecular analogues *syn*- and *anti*-**2m** and **n**. Finally, the grafting of **1** onto silica involves the reaction of both the alkyl and the alkylidene ligand with an equiprobability, leaving the alkylidyne as a spectator ligand. Noteworthy is the formation of **2** [(≡SiO)Re(≡C^{t}Bu)(=CH^{t}Bu)(CH$_2$^{t}Bu)], rather than the corresponding trisneopentyl-neopentylidyne Re complex, monografted on silica, [(≡SiO)Re(≡C^{t}Bu)(CH$_2$^{t}Bu)$_3$], which would have been expected from the reactivity of **1** with various molecular Brönsted acids and which also suggests that a proximal siloxane bridge forces the α-H abstraction process, leading to *syn*-**2a**.

Introduction

In our continuous effort to study the interaction of organometallic complexes with oxide supports such as silica, we have recently disclosed the outcome of the reaction of **1a** [Re(≡C-^{t}Bu)(=CH^{t}Bu)(CH$_2$^{t}Bu)$_2$][1] with a silica partially dehydroxylated at 700 °C, that is, the formation of a well-defined surface alkylidene complex obtained as a single isomer: [(≡SiO)Re-(≡C^{t}Bu)(=CH^{t}Bu)(CH$_2$^{t}Bu)] (*syn*-**2a**) (Scheme 1).[2] The relative and rather unexpected simplicity of the coordination sphere obtained on a silica support is worth pointing out because organometallic Re complexes have a large palette of potential reactivities and structural isomerisms; it is therefore of great interest to analyze the differences and similarities between **2a** and molecular Re complexes. We decided (i) to further investigate the structural identity of **2a** and its stability, and (ii) to understand the mode − mechanism − of grafting of **1a** onto silica to compare the reactivity of organometallic complexes with surfaces and that of molecular complexes in solution.

Scheme 1. Grafting of **1a** onto Silica Partially Dehydroxylated at 700 °C



Results and Discussion

Mass Balance Analysis. The preparation of **2a** involves the reaction of **1a** in solution in pentane for 2 h with a silica partially dehydroxylated at 700 °C ($SiO_{2-(700)}$). Typically Re is grafted in 3.9−4.7%$_{wt}$ depending on the batch of silica used (Table 1),

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(1) For the preparation of **1a**, see: (a) Edwards, D. S.; Biondi, L. V.; Ziller, J. W.; Churchill, M. R.; Schrock, R. R. *Organometallics* **1983**, *2*, 1505. (b) Toreki, R.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 3367.
(2) Chabanas, M.; Baudouin, A.; Copéret, C.; Basset, J.-M. *J. Am. Chem. Soc.* **2001**, *123*, 2062.

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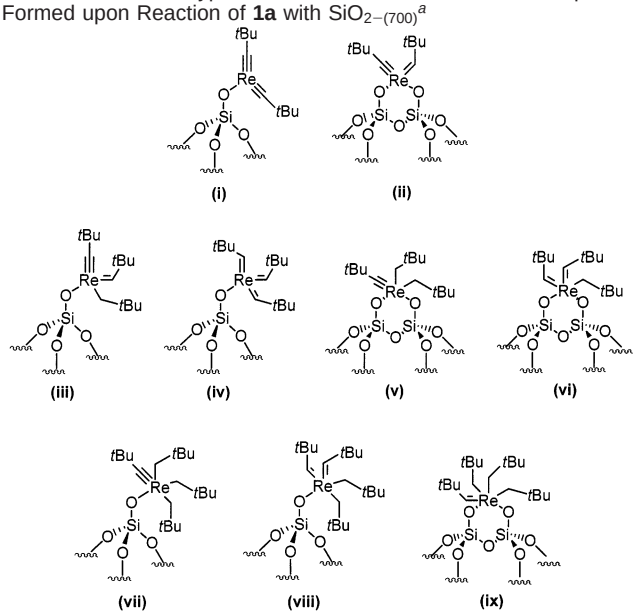
Table 1. Grafting of **1a** onto Silica Partially Dehydroxylated at 700 °C

impregnation	%$_w$Re[a]	NpH/Re (grafting)[b]	%$_w$C[a]	C/Re (Np$^{\#}$/Re[c])	Np$^{\#}$/Re[d] (hydrogenolysis)
1	4.71	1.03	4.54	15.0 (3.00)	
2	4.16		4.55	17.0 (3.40)	
3	4.24	1.10			
4	4.03	1.08			
5	4.00	1.08			2.95
6	4.75	0.79	4.55	14.9 (2.98)	2.83
7	3.95	1.07	4.01	15.8 (3.16)	2.89
8[e]	3.52	1.27	3.51	15.5 (3.09)	3.74
9[e]	3.50	1.03	3.33	14.8 (2.96)	

[a] Elemental analysis. [b] Neopentane (NpH) released during the grafting, quantified by GC. [c] Number of neopentyl-like ligands (Np$^{\#}$) present on average in the coordination sphere of Re, determined by elemental analysis. [d] Average number of neopentyl-like ligands (Np$^{\#}$) around Re, determined by quantifying CH_4 produced during the hydrogenolysis of the solid, Np$^{\#}$/Re = (CH_4/Re)/5. [e] Surface not saturated due to a lack of **1a** in the pentane solution.

which corresponds to the consumption of 0.21−0.26 mmol/g of silanol groups and to the amount of silanols accessible for bulky complexes on a silica partially dehydroxylated at 700 °C.[3] Moreover, the amount of neopentane evolved during grafting is on average 1.06 ± 0.13 mol per grafted Re on the surface, in agreement with the replacement of one neopentyl ligand of **1a** by a siloxy ligand of the surface. The corresponding grafted organometallic compound contains 15.5 ± 0.8 carbons per grafted Re according to elemental analysis, that is, the equivalent of 3.1 ± 0.2 "neopentyl-like" ligands (Np$^{\#}$).[4] Additionally, the hydrogenolysis of **2a** at 250 °C for 2−4 days liberated 14.5 ± 0.3 methane/Re along with the complete disappearance of typical alkyl stretching frequencies in the 2800−3000 cm^{-1} region according to in situ-IR spectroscopy. This is accompanied with the partial recovery of silanol groups, which probably implies that some Re−O bonds with the support are cleaved under these conditions to form Re particles. Nonetheless, the amount of methane formed can be related to the number of carbons or "neopentyl-like" ligands around the Re center, that is, an average of 2.9 ± 0.1 Np$^{\#}$/Re, which is in close agreement with elemental analysis data. Therefore, this set of data is consistent with the loss of approximately 1 equiv of neopentane during the grafting, leaving on average three "neopentyl-like" ligands around the metal center. On the basis of these data alone, it is possible to propose several surface complexes, as well as mixtures of surface complexes (Scheme 2).

Scheme 2. Some Hypothetical Structures for the Surface Species Formed upon Reaction of **1a** with $SiO_{2-(700)}$[a]



[a] Structures involving three bonds to the surface are omitted because the probability of forming such a species on $SiO_{2-(700)}$ is very low.

1D and 2D Solid-State NMR Spectroscopy. We have already reported the ^{1}H NMR solid-state NMR of **2**, which shows signals at 11.0 and 1.0 ppm along with two other signals of less intensity at 3.0 and 2.6 ppm.[2] At natural abundance, the sensitivity of the ^{13}C CP/MAS experiment is too low to adjust properly the experimental parameters of the CP and to obtain a signal within a reasonable experimental time. However, we have shown that it is possible to characterize the carbon spectrum by labeling **2a** to the extent of 10% on all carbons in the α-position to the metal center (**2b**). Signals in the carbon CP/MAS spectrum at 29, 46, and 246 ppm were observed and

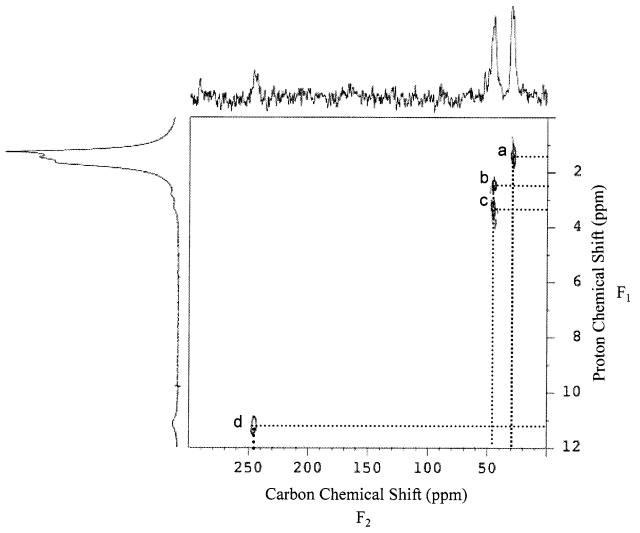


Figure 1. ^{1}H−^{13}C HETCOR solid-state NMR spectra of the Re surface species **2b** using a contact time for the cross-polarization of 0.5 ms.

assigned to **C**H_3, **C**H_2^{t}Bu, and =**C**H^{t}Bu resonances, respectively. An extra signal was observed at 292 ppm, when using direct carbon excitation, which was attributed to the (≡**C**^{t}Bu) resonance (vide infra Figure 4b). These assignments were exclusively based on the comparison with chemical shifts obtained from a molecular analogue **2m** [Ph_3SiORe(≡C^{t}Bu)(=CH^{t}Bu)(CH_2^{t}Bu)] prepared by the reaction of triphenylsilanol and **1a** (vide infra Scheme 4, Table 2, and **4**−**5**). Nevertheless, it would be desirable to obtain more direct evidence that would confirm these assignments. Recently, we have shown that 2D HETCOR (heteronuclear correlation) solid-state NMR using magic angle spinning (MAS) can be used in the same way as solution-state experiments to clearly ascertain chemical shift assignments.[5] The 2D ^{1}H−^{13}C HETCOR MAS NMR spectrum

(3) Chemical titration and numerous data obtained for the grafting of other perhydrocarbyl complexes of Ti (1.3%$_{wt}$, 0.27 mmol/g), Zr (2.3%$_{wt}$, 0.25 mmol/g), Hf (4.2% $_{wt}$, 0.24 mmol/g), Ta (4.2% $_{wt}$, 0.24 mmol/g), and Mo (2.1%$_{wt}$, 0.22 mmol/g) onto $SiO_{2-(700)}$ show the presence of around 17−0.27 mmol of accessible SiOH groups per gram of $SiO_{2-(700)}$.

(4) By "neopentyl-like", we mean either neopentyl-, neopentylidene-, or neopentylidyne-type ligands.

(5) (a) Petroff Saint-Arroman, R.; Chabanas, M.; Copéret, C.; Basset, J.-M.; Lesage, A.; Emsley, L. *J. Am. Chem. Soc.* **2001**, *123*, 3082. (b) Chabanas, M.; Quadrelli, A.; Copéret, C.; Thivolle-Cazat, J.; Basset, B.; Fenet, J.-M.; Lesage, A.; Emsley, L. *Angew. Chem., Int. Ed.* **2001**, *43*, 4493.

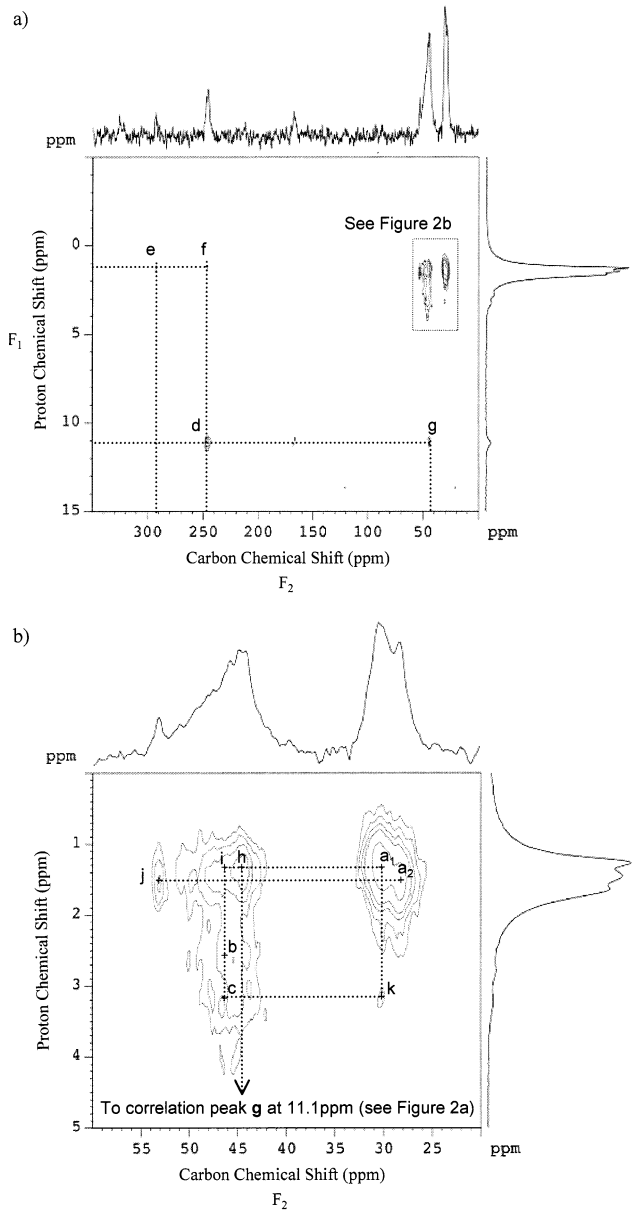


Figure 2. $^{1}H-^{13}C$ HETCOR solid-state NMR spectra of the Re surface species **2b** using a contact time for the cross-polarization of 5 ms: (a) Full spectrum. (b) Expanded region.

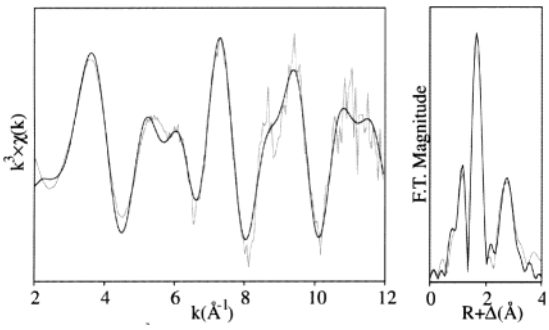
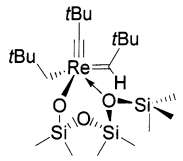


Figure 3. Re L_{III}-edge k^3-weighted EXAFS (left) and Fourier transform (right) of **2a**: gray lines, experimental; black lines, spherical wave theory.

of **2b** recorded with a contact time of 0.5 ms (Figure 1) shows a correlation (a) between protons around 1.4 ppm and carbons around 29 ppm. Moreover, the ^{13}C resonance of the methylene group of the neopentyl ligand ($\mathbf{C}H_2{}^t$Bu, 45−46 ppm) gives two

Scheme 3. Proposed Structure Combining Solid-State NMR and EXAFS Data



correlations (b and c) with protons at about 2.6 and 3.2 ppm, which correspond to the two diastereotopic protons ($C\mathbf{H_A}\mathbf{H_B}{}^t$Bu), previously reported in the 1D ^1H spectrum at 2.6 and 3.1 ppm. Finally, a correlation peak (d) can be observed between the proton at 11.1 ppm and the carbon at 246 ppm, confirming the assignment of these signals to the carbenic proton and carbon, respectively (=C**H**^{t}Bu). Note that, in this case, the use of a contact time of 0.5 ms allows the selective observation of C−H nuclei which are spatially very close (i.e., directly bonded). Under these conditions of relatively short contact time, a solid-state HETCOR experiment can be interpreted much like analogous HETCOR experiments in solution NMR (also called H−C COSY or HSQC), although the pulse sequence and magnetization transfer mechanism involved in these two sequences are completely different (the transfer is mediated by through-space dipolar interactions in solids versus through-bond scalar couplings in liquids).[6] Using longer contact times (>1 ms), we found that it is possible to observe extra correlation peaks, which arise from longer range dipolar through-space interactions. These long-range spectra yield further information about the structure of **2a**. The $^1H-^{13}C$ HETCOR spectrum of **2b** was therefore recorded with a contact time of 5 ms (Figure 2a,b). The expanded view of the aliphatic region in Figure 2b shows that the correlation peak called "a" appeared in this spectrum as two well-separated components a_1 (1.4 ppm; 30 ppm) and a_2 (1.6 ppm; 28 ppm). In fact, the correlation peak a_1 corresponds to two correlations, but the resolution and the chemical shift difference are not sufficient to clearly identify each of them. The correlation peak g (11.1 ppm; 44 ppm) corresponds to the interaction of the carbenic proton with a carbon at 44 ppm, which must be relatively close, probably the quaternary carbon of the neopentylidene ligand (=CH**C**$(CH_3)_3$). This carbon at 44 ppm also correlates with a proton at around 1.4 ppm (h), which could therefore be assigned to the methyl resonance of the neopentylidene ligand (=CHC($C\mathbf{H}_3)_3$). The signal in F_1 around 1.4 ppm also corresponds to the methyl resonance of the neopentyl ligand ($CH_2C(C\mathbf{H}_3)_3$) because it correlates (peak i) with the carbon at 46 ppm ($\mathbf{C}H_2{}^t$Bu). Therefore, the correlation peak a_1 probably corresponds to the two methyl groups of both the neopentyl and the neopentylidene ligands. As a consequence, a_2 (1.6 ppm, 28 ppm) could be assigned to the methyl group of the neopentylidyne ligand (≡CC($\mathbf{C}H_3)_3$). The corresponding proton resonance at 1.6 ppm ((≡CC($C\mathbf{H}_3)_3$) clearly correlates with a sharp signal at 53 ppm (peak j), probably the quaternary carbon of the neopentylidyne ligand (≡C**C**$(CH_3)_3$). Noteworthy is also the correlation (peak k) of only one of the diastereotopic protons at 3.1 ppm with a carbon at 30 ppm, which can be assigned to either a carbon of a methyl group ($CH_2C(\mathbf{C}H_3)_3$) or, more likely, the quaternary carbon α to the methylene ($CH_2\mathbf{C}(CH_3)_3$), as observed on the neopentylidene and neopentylidyne ligands. The other two

(6) Derome, A. E. *Modern NMR Techniques for Chemistry Research*; Organic Chemistry Series Vol. 6; Pergamon Press: Oxford, 1987.

Table 2. Discernible ^{1}H and ^{13}C NMR Resonances for the Surface Compound *syn*-**2b**

^{1}H NMR, δ/ppm		^{13}C NMR, δ/ppm[a]	
resonances	assignments	resonances	assignments
1.1	C(C**H**$_3$)$_3$)	28	≡CC(**C**H$_3$)$_3$
1.3	C(C**H**$_3$)$_3$)	30	C(**C**H$_3$)$_3$)
1.5	≡CC(C**H**$_3$)$_3$)	30	CH$_2$**C**(CH$_3$)$_3$)
2.6	C**H**$_A$H$_B$^{t}Bu	44	=CH**C**(CH$_3$)$_3$)
3.1	CH$_A$**H**$_B$^{t}Bu	46	**C**H$_2$^{t}Bu
11.1	=C**H**^{t}Bu	53	≡C**C**(CH$_3$)$_3$)
		246	=**C**H^{t}Bu
		292	≡**C**^{t}Bu

[a] Some data are assigned via 2D HETCOR solid-state NMR.

Table 3. EXAFS Parameters for **2a**[a]

element	# of atoms	distance (Å)[b]	Debye–Waller factor (Å^2)[b]	assignment
C	2	1.789(4)	0.0125(4)	Re≡**C**C(Me)$_3$ Re=**C**HC(Me)$_3$
O	1	2.015(3)	0.0056(2)	Re−**O**Si≡
C	1	2.015[c]	0.0056[c]	Re−**C**H$_2$C(Me)$_3$
O	1	2.420(8)	0.012(1)	Re←(**O**Si$_2$) Re≡C**C**(Me)$_3$
C	3	3.286(5)	0.0044(4)	Re=CH**C**(Me)$_3$ Re−CH$_2$**C**(Me)$_3$

[a] E_0 for all shells is −6.9(5) eV. [b] Number in parentheses is the standard deviation of the parameter in the fit. [c] Parameter linked to the preceding shell.

methyl groups from the ^{t}Bu fragments of the neopentyl and neopentylidene ligands cannot be fully assigned under these conditions. Nevertheless, combining the information given by 1D and 2D solid-state NMR spectroscopy provides a relatively complete NMR data set for the surface compound **2a**. All of these data are fully consistent and indicate that the reaction of **1a** with $SiO_{2-(700)}$ leads to the formation of [(≡SiO)−Re(≡C-^{t}Bu)(=CH^{t}Bu)(CH$_2$^{t}Bu)], **2a**, as the sole surface species (Scheme 1 and Table 2).

EXAFS Data. EXAFS data collected from the Re surface complex **2a** (Figure 3) are consistent with the NMR data with one difference: a dative bond from a siloxane bridge can also be observed. The parameters derived from fitting the EXAFS data (Table 3) describe the local environment of the rhenium center. The distances to the two nearest carbon neighbors, corresponding to the (=**C**H^{t}Bu) and (≡**C**^{t}Bu) ligands, cannot be resolved with the data range available. The large Debye−Waller factor for this shell is consistent with this assignment. Similarly, the (−**O**Si≡) and −**C**H$_2$^{t}Bu cannot be resolved and were fit using two shells with the same parameters. The 1.79 Å distance for the first shell is consistent with an average of Re−C distances in alkylidene and alkylidyne complexes of Re^{VII}: 1.85−1.89 C and 1.74−1.76 Å, respectively,[7] and the 2.01 Å distance for the second shell is consistent with an average of Re−O and Re−C distances in Re^{VII} complexes: 1.90−2.00 Å[7] and 2.11 Å,[8] respectively. Moreover, an extra atom, oxygen, is also present in the coordination sphere of Re, at a longer Re−O distance (2.42 Å), which is most likely due to a dative bond from an adjacent siloxane bridge because it is similar to that of the Re−OC$_4$H$_8$ (THF, 2.398 Å) in *syn*-Re(≡C^{t}Bu)(=CH^{t}Bu)-[OCMe(CF$_3$)$_2$](THF).[9] Therefore, these data are most consistent with the presence of an extra siloxane bridge as a two-electron donor ligand.[10] The large Debye−Waller factor suggests that either only some of the surface complexes possess this bond or, more likely, a large variation of (Re−O) bond lengths is present (heterogeneity of the silica surface). The final component is due to scattering from the *tertiary* carbon atoms of the ligands. Additional scattering shells due either to multiple scattering or to scattering from Si in the support do not significantly improve the fit of the model to the data. Overall, the EXAFS data are in excellent agreement with the structure of **2** with an additional dative bond from a siloxane bridge in the silica support as shown in Scheme 3.

Syn−Anti Isomerism, A Comparison with Molecular Complexes. Rotational isomers (rotamers) are common in the organometallic chemistry of alkylidene complexes. The alkylidene substituent can indeed be pointed either toward (syn) another multiply bonded ancillary ligand (imido, alkylidyne, etc.) or away (anti) from it. Some alkylidene organometallic syntheses yield only one rotamer (usually the syn one), which can be generally converted into a mixture of the syn and the anti rotamers either thermally or photochemically. An interesting example is the molecular complex *syn*-[Re(≡C^{t}Bu)(=CH^{t}Bu)-(OR$_F$)$_2$],[1b] whose chemical structure is quite similar to that of **2a**. The reaction of **1a** with 1 equiv of Ph$_3$SiOH in benzene at room temperature quantitatively gives neopentane and **2m** [Ph$_3$-Si−O−Re(≡C^{t}Bu)(=CH^{t}Bu)(CH$_2$^{t}Bu)] (see Supporting Information). Very similar NMR data were obtained for another molecular model **2n** [(*c*-C$_5$H$_9$)$_7$Si$_7$O$_{12}$Si−O−Re(≡C^{t}Bu)(=CH^t-Bu)(CH$_2$^{t}Bu)], prepared by the reaction of **1a** with the poly-oligomeric silsesquioxane **3** [(*c*-C$_5$H$_9$)$_7$Si$_7$O$_{12}$Si−OH]. These complexes are rather unstable as compared to their surface complex analogue, which has so far prevented us from obtaining suitable crystals for X-ray analysis (slow decomposition at room temperature in our hands). Additionally, they are obtained as a 10/1 mixture of syn and anti rotamers along with about 1 equiv of neopentane (Scheme 4). The surface complex **2a** has chemical shift values very close to those obtained for syn isomers, which further points out that **2a** is obtained as the syn isomer, as the sole surface species.

When the surface complex *syn*-**2b** was heated at 120 °C under Ar during 30 min, typical signals for *syn*-**2b** were still present in both ^{1}H and ^{13}C spectra, but a new signal at 12.6 ppm (in the carbenic proton range) was observed in the MAS ^{1}H NMR (Figure 4c), and extra peaks at 68, 257, and 302 ppm were also detected by direct excitation solid-state ^{13}C NMR spectroscopy (Figure 4d). The extra signal at 12.6 ppm in the MAS ^{1}H NMR spectrum matches the carbenic proton signal of the anti isomer of the molecular models (12.65 ppm for *anti*-**2m** and 12.63 ppm for *anti*-**2n**, Figure 5 (and Supporting Information) for comparison). Moreover, the extra signals at 257 and 302 ppm in ^{13}C solid-state NMR also match, respectively, the carbenic and the carbynic signals of the anti isomers of the molecular models, providing good evidence for the partial isomerization of the surface complex *syn*-**2b** into its anti rotamer, *anti*-**2b**.[11,12]

(7) For Re−O, Re=C, and Re≡C bond distances, see: (a) ref 1. (b) Cai, S.; Hoffman, D. M.; Wierda, D. A. *J. Chem. Soc., Chem. Commun*. **1988**, 1489. (c) Toreki, R.; Schrock, R. R.; Vale, M. G. *J. Am. Chem. Soc*. **1991**, *113*, 3610. (d) Toreki, R.; Vaughan, G. A.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc*. **1993**, *115*, 127.

(8) For a Re−C bond distance, see ref 7b.

(9) Schofield, M. H.; Schrock, R. R.; Park, L. Y. *Organometallics* **1991**, *10*, 1844. See also refs 1a and 7d.

(10) Similar observations have been made on other grafted organometallic complexes, see: Corker, J.; Lefebvre, F.; Lécuyer, C.; Dufaud, V.; Quignard, F.; Choplin, A.; Evans, J.; Basset, J.-M. *Science* **1996**, *271*, 966. Vidal, V.; Théolier, A.; Thivolle-Cazat, J.; Basset, J.-M.; Corker, J. *J. Am. Chem. Soc.* **1996**, *118*, 4595.

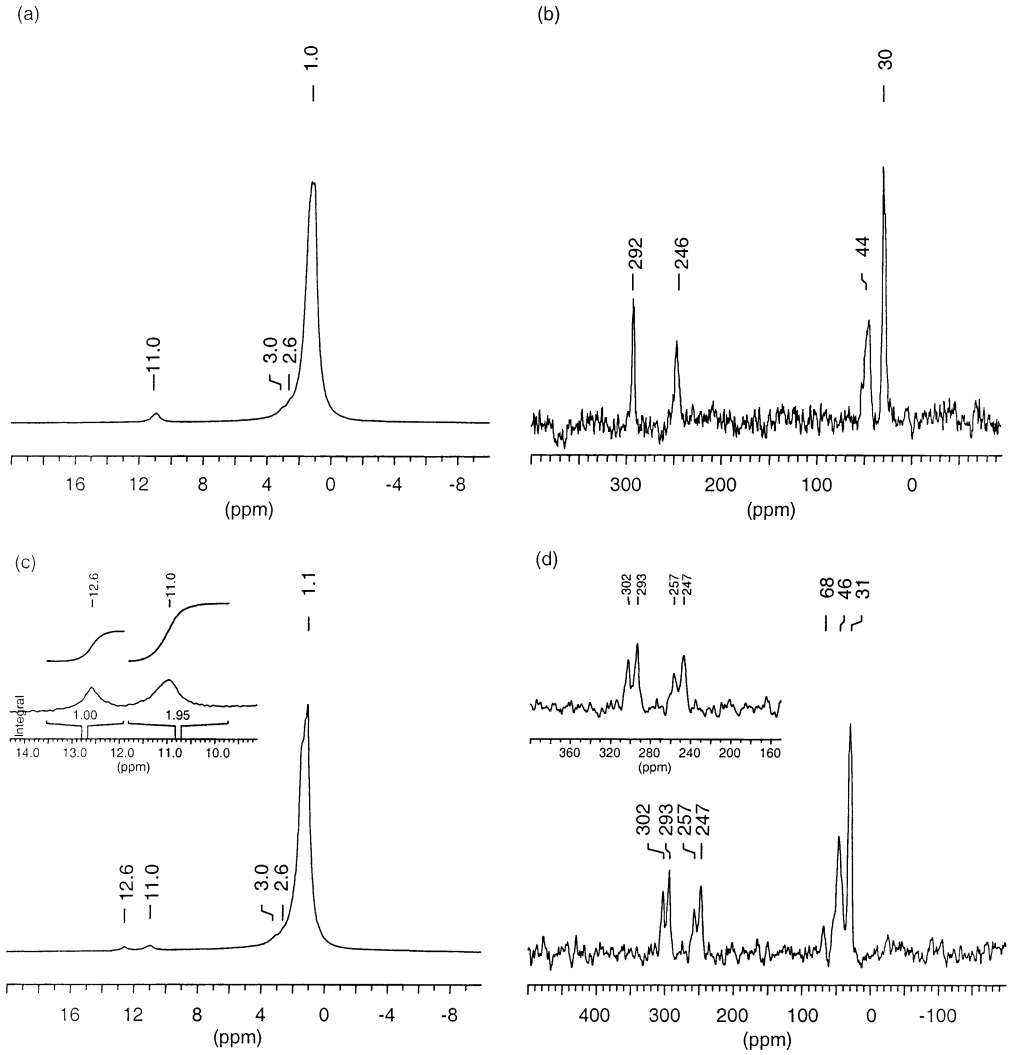
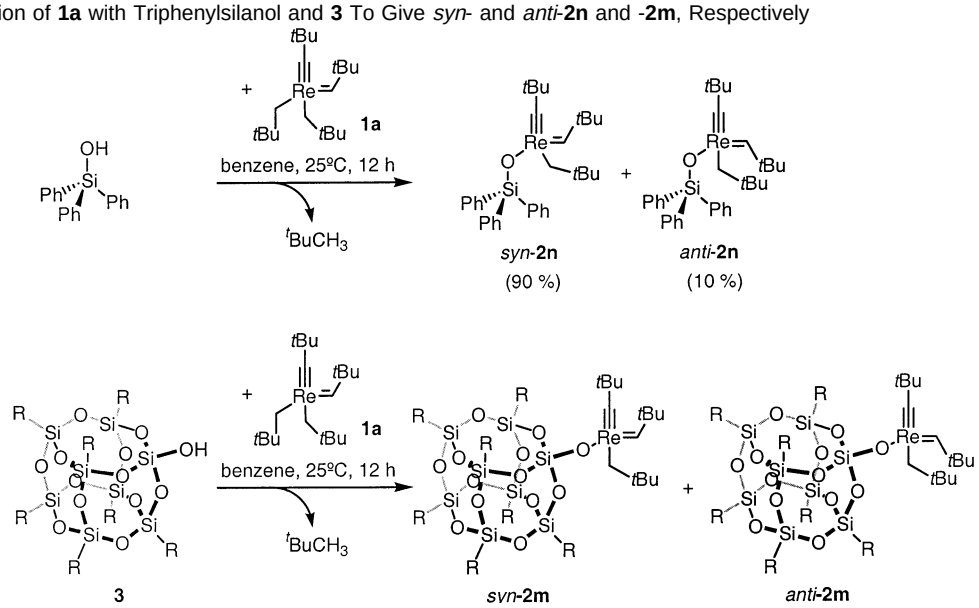


Figure 4. MAS ^{1}H and HPDEC ^{13}C solid-state NMR spectra of **2b** before ((a) and (b)) and after ((c) and (d)) heating at 120 °C under argon for 30 min. Spectra recorded at 25 °C.

Scheme 4. Reaction of **1a** with Triphenylsilanol and **3** To Give *syn*- and *anti*-**2n** and -**2m**, Respectively



These assignments were further confirmed by 2D HETCOR solid-state NMR (Figure 6). Integration of the carbenic proton peaks over several experiments (120 °C, 30 min) gave a syn/anti ratio of approximately 2.0 ± 0.5. Almost the same NMR spectrum with a measured syn/anti ratio of 2.0 was obtained for a sample treated for a longer time (1 h 25 min) at 120 °C.

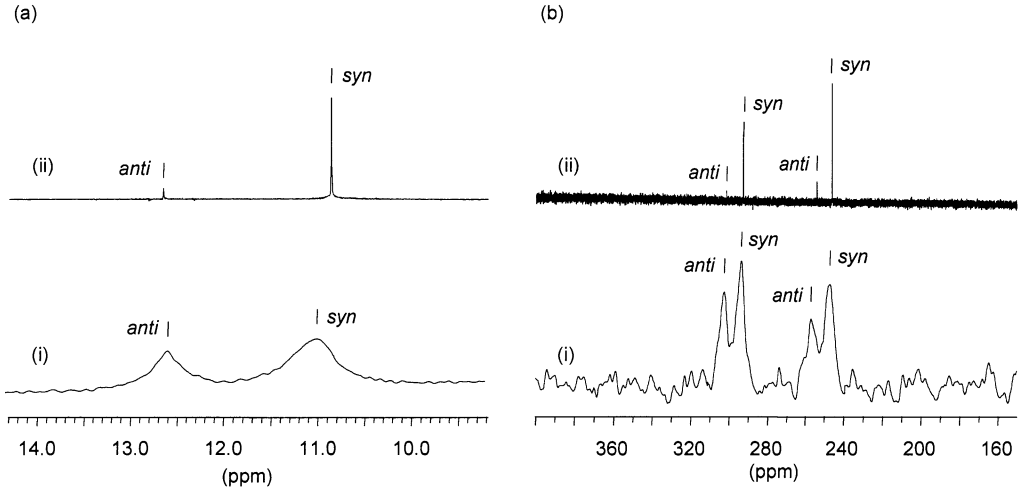


Figure 5. Direct comparison of NMR data for syn and anti rotamers of both the surface complex **2b** [(≡SiO)−Re(≡C^{t}Bu)(=CH^{t}Bu)(CH$_2$^{t}Bu)] (i) and the molecular model **2m** [Ph$_3$SiO)−Re(≡C^{t}Bu)(=CH^{t}Bu)(CH$_2$^{t}Bu)] (ii). (a) ^{1}H NMR (carbenic region). (b) ^{13}C NMR (carbenic and carbynic region).

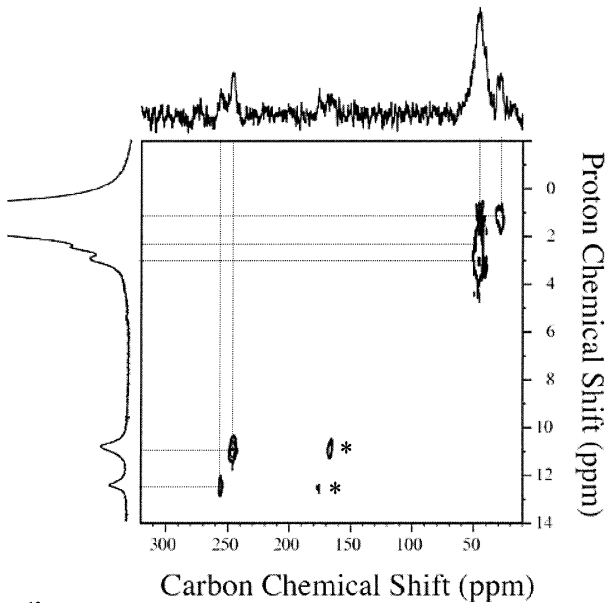
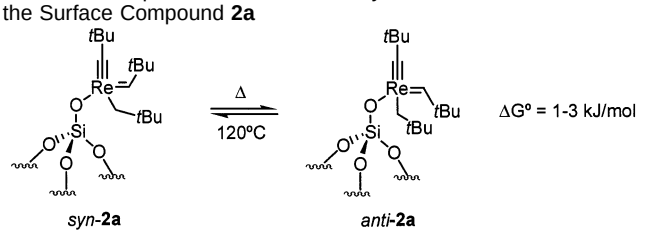


Figure 6. ^{1}H−^{13}C HETCOR solid-state NMR spectra of the Re surface species *syn*- and *anti*-**2b** using a contact time for the cross-polarization of 0.5 ms. * notes the correlation peaks with spinning side bands.

Scheme 5. Equilibrium between the Syn and the Anti Rotamers of the Surface Compound **2a**



This shows that the syn/anti ratio of 2.0 corresponds to a stabilized composition at this temperature.

In situ solid-state NMR experiments provided further information about this isomerization. A rotor, filled with pure *syn*-**2a**, was heated in the NMR probe at 60 °C[13] for 30 min, and MAS ^{1}H NMR spectra were recorded at this temperature, giving a new carbenic signal at 12.5 ppm. Upon cooling, the relative intensities of the peaks at 11 and 12.5 ppm did not change. Finally, no syn−anti isomerization of **2a** was observed at 25 °C over a 12−48 h period according to ^{1}H NMR. Similarly, the syn/anti ratio measured at 25 °C for the molecular model **2m** (reaction of **1a** with Ph$_3$SiOH at 25 °C) did not vary, even after prolonged storage in the dark at 25 °C (syn/anti = 10). All of these data are consistent with a very slow transformation of the syn to the anti rotamer of **2a** at 25 °C. The isomerization becomes observable at higher temperatures (Scheme 5). Therefore, the syn/anti ratio of 2.0 ± 0.5 measured at 25 °C after treatment at 120 °C (67 ± 7% syn, 33 ± 7% anti) corresponds probably to the thermodynamic equilibrium at 120 °C. $\Delta G°$ of this transformation can be measured to be +2 ± 1 kJ/mol at 120 °C.

Interestingly, storage of **2a** for 24 h at 25 °C in a Pyrex Schlenk tube exposed to daylight also induced syn−anti isomerization. After this treatment, approximately 40% of *syn*-**2a** was converted into *anti*-**2a** (syn/anti = 1.52). In conclusion, **2a** can be indeed present as two different rotational isomers, as for analogous molecular complexes, but is generated selectively as the syn rotamer upon grafting. It is probably the kinetic product even though our data do not allow us to certify it.

Investigation of the Grafting Mechanism. Because three types of perhydrocarbyl ligands (neopentyl, neopentylidene, and neopentylidyne) are present in the molecular precursor **1a**, several mechanisms for the grafting could in principle occur (Scheme 6): (i) direct cleavage of the Re−C bond of the neopentyl ligand by a silanol O−H bond (electrophilic cleavage), (ii) addition of a silanol O−H bond onto the neopentylidene moiety followed by α-H abstraction, and/or (iii) addition of a silanol O−H bond onto the neopentylidyne moiety followed by α-H abstraction.

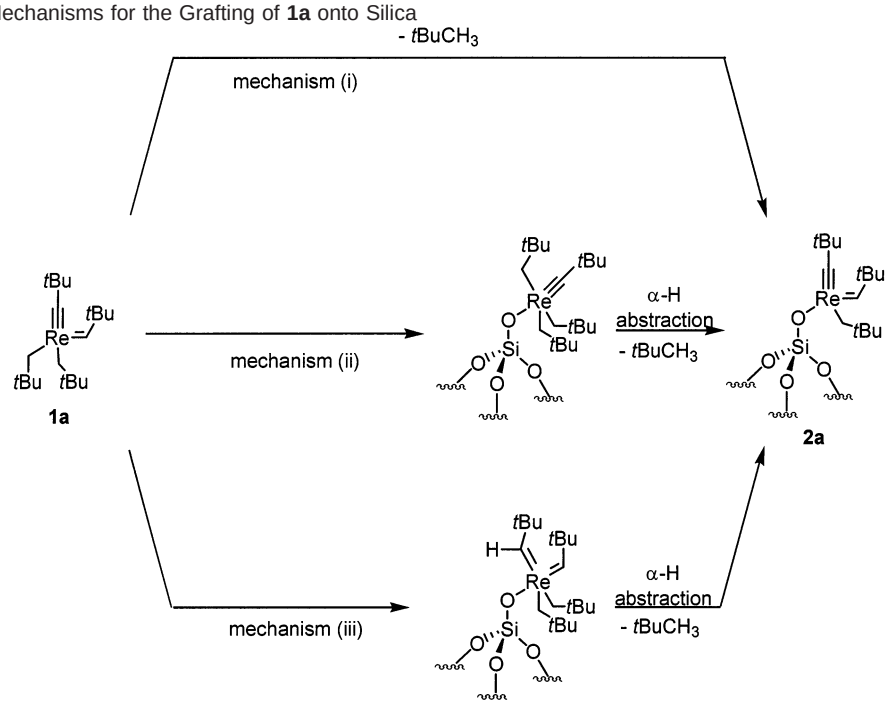
One should note at this point that the preparation of **1a** involves two distinct alkylation steps with [Mg(CH$_2$^{t}Bu)Cl], allowing in principle for the introduction of first the alkylidyne

(11) In four-coordinate d^0 species, syn alkylidenes exhibit a lower $^1J_{CH}$ coupling constant and upfield ^{1}H and ^{13}C NMR resonances relative to the anti rotamer. Re^{VII}: see ref 1b. Mo^{VI} : Oskam, J. H.; Schrock, R. R. *J. Am. Chem. Soc*. **1993**, *115*, 11831. See also: LaPointe, A. M.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1995**, *117*, 4802 and references therein.

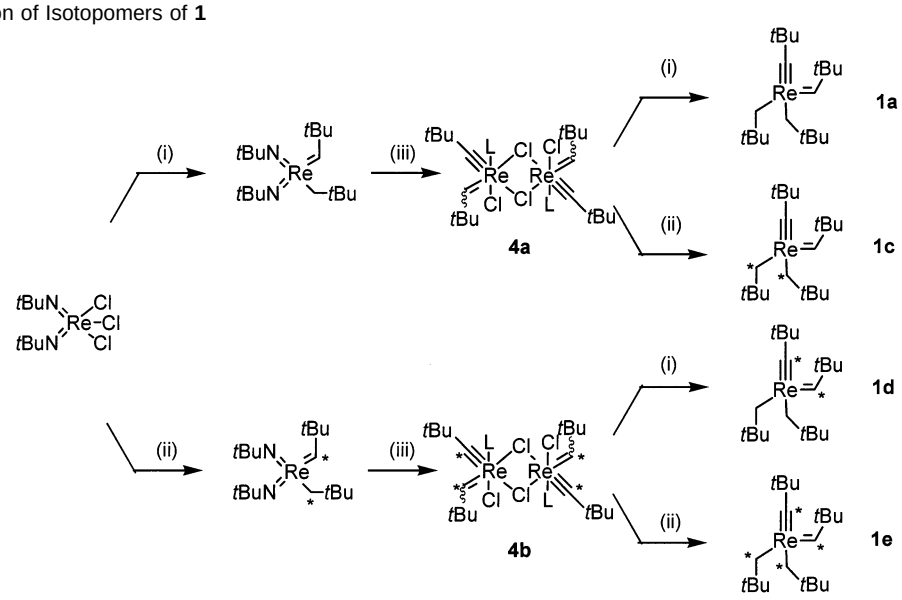
(12) The signal for **C**H$_2$^{t}Bu of *anti*-**2b**, which should appear around 47 ppm (according to the model compound), is probably buried under the broad **C**H$_2$^{t}Bu signal of *syn*-**2b** (44 ppm). The extra peak at 68 ppm is probably due to a partial decomposition of the product because it does not appear reproducibly.

(13) The actual temperature in the probe is probably much higher that the one fixed (>100 °C).

Scheme 6. Possible Mechanisms for the Grafting of **1a** onto Silica



Scheme 7. Preparation of Isotopomers of **1**



and the alkylidene, and then the two alkyl moieties (Scheme 7). This strategy allows in principle the selective synthesis of four distinct isotopomers depending on the use of [Mg($CH_2{}^t$Bu)Cl] and/or [Mg($^{13}CH_2{}^t$Bu)Cl] for each alkylating step. Therefore, it is possible to generate the unlabeled or fully ^{13}C-labeled dimers, **4a** and **4b**, respectively, which can in turn be transformed via a second alkylation step into **1a** (unlabeled), **1c** (dilabeled, selectively on the two alkyl ligands), **1d** (dilabeled, selectively on the alkylidene and alkylidyne ligands), and **1e** (tetralabeled), depending on the use of a labeled or unlabeled Grignard reagent at each alkylation step. While the synthesis of **1a** and **1e** provided the expected isotopomers, the selectivity in the formation of **1c** and **1d** was only partial. Therefore, **1c** was obtained with 92 and 15% incorporation of ^{13}C labeling in the methylene (**C**$H_2{}^t$Bu) and the methine (=**C**H^{t}Bu) carbons, respectively, with no labeling in the alkylidyne carbon (≡**C**-^{t}Bu), while **1d** was obtained with 27, 65, and >85% incorporation of ^{13}C labeling in the methylene (**C**$H_2{}^t$Bu), the methine (=**C**H^{t}Bu), and the alkylidyne (≡**C**^{t}Bu) carbons, respectively. This shows that the second step of alkylation is probably not very selective.

The alkylidene and alkyl ligands can interexchange readily under the reaction conditions, probably via H-transfer,[14] while the alkylidyne seems reluctant to participate in such a process; hence no incorporation of ^{13}C (via an exchange process) in this ligand is observed.[15] To have an estimation of the stability of the isotopomer composition, a 0.1 M solution in C_6D_6 of **1c**

(14) Schrock, R. R.; Clark, D. N.; Sancho, J.; Wengrovius, J. H.; Rocklage, S.; Pedersen, S. F. *Organometallics* **1982**, *1*, 4802. Caulton, K. G.; Chilsom, M. H.; Streib, W. E.; Xue, Z. *J. Am. Chem. Soc.* **1991**, *113*, 6082. Lapointe, A. M.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1995**, *117*, 4802. Li, L.; Hung, M.; Xue, Z. *J. Am. Chem. Soc.* **1995**, *117*, 12746. Chen, T.; Wu, Z.; Li, L.; Sorasaenee, K. R.; Diminie, J. B.; Pan, H.; Guzei, I. A.; Rheingold, A. L.; Xue, Z. *J. Am. Chem. Soc.* **1998**, *120*, 13519.

(15) No ^{13}C-enrichment of the alkylidyne carbon was detected by NMR spectroscopy (<2% ^{13}C).

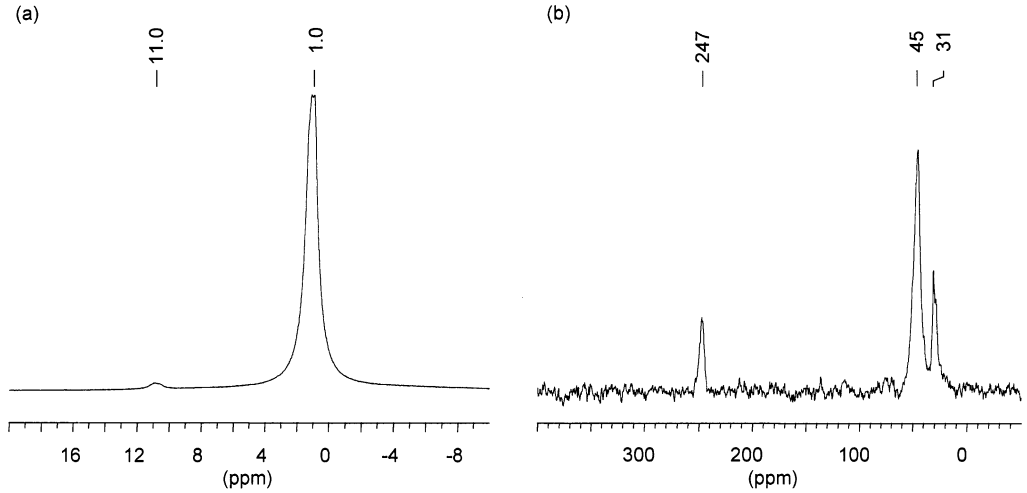


Figure 7. (a) MAS ^{1}H and (b) HPDEC ^{13}C solid-state NMR of **2c**.

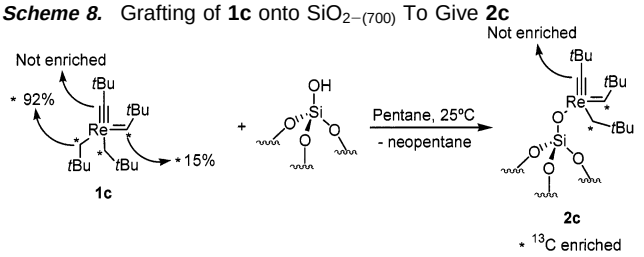
was stored at 25 °C in the dark, and the isotopic composition was measured regularly over a 2-month period by ^{1}H NMR spectroscopy. The percentage of ^{13}C-label on the methylene carbon slowly decreased, whereas the percentage of ^{13}C-label in the carbenic carbon increased.[16] Interestingly, the singlet for the methyl group of the neopentylidyne (1.38 ppm) did not change, showing that no ^{13}C-enrichment occurs on the carbynic ligand. Integration of the carbenic signals gives the percentage of ^{13}C incorporated into the carbenic moiety. The isotopic composition stabilized after 1000 h (about 1.5 months!) when the carbenic carbon and the methylene carbons were ^{13}C-enriched to 64 and 68%, respectively. The alkylidyne ligand was still not enriched (<2%). This corresponds to a quasi statistical redistribution of the ^{13}C label over alkyl and alkylidene ligands (that is, about 66% ^{13}C enrichment on each position). α-H transfer reactions can readily account for these observations.[13] According to our data, only the transfer of a methylene proton (of the neopentyl) to the alkylidene moiety takes place, while the alkylidyne is a spectator ligand and does not participate in α-H transfer reactions.[17] It is worth noting that the isotopomer distribution can be considered stable on the reaction time scale used for impregnation. Therefore, the grafting of **1c** onto $SiO_{2-(700)}$ gave the surface product **2c**. CP/MAS and especially a direct excitation ^{13}C solid-state NMR spectrum show absolutely no carbynic resonance (Figure 7), even though the pulse sequence and the parameters used were those known to favor the observation of carbynic resonances.

This rules out the participation of mechanism (iii) in the grafting of **1a** because it implies first the formation of an intermediate containing two alkylidene ligands, of which one would be partially ^{13}C-labeled thus leading to scrambling in the α-H abstraction step (Scheme 8). No strong ^{12}C/^{13}C isotopic effect is expected for the α-H abstraction step, and therefore if mechanism (iii) were operating, we would have observed at least a partial ^{13}C enrichment of the carbynic ligand during the grafting. The absence of labeling (<5%) in the alkylidyne ligand in the surface species shows that the carbyne in **1c** is a spectator

(16) A partially deuterated analogue, Re(≡C^{t}Bu)(=CH^{t}Bu)(CD$_2$^{t}Bu)$_2$ has shown no evidence for H/D scrambling among the neopentyl and neopentylidene ligands at 80 °C in toluene-d_8, see: Lapointe, A. M.; Schrock, R. R. *Organometallics* **1995**, *14*, 1875.

(17) In Re(≡C^{t}Bu)(=CH^{t}Bu)(OR)$_2$, the alkylidyne ligand was found to behave in most cases as an ancillary ligand, see ref 7c.

Scheme 8. Grafting of **1c** onto $SiO_{2-(700)}$ To Give **2c**



ligand during the grafting (Scheme 8). The molecular precursor **1c** is partially ^{13}C-enriched on the alkyl and alkylidene ligands to 92 and 15%, respectively. The isotopic distribution of the neopentane released during its grafting onto $SiO_{2-(700)}$ should provide information about the grafting mechanism involved (eq 1).

The relative importance of pathways (i) and (ii) can be in principle estimated (eqs 1 and 2) using the percentage of ^{13}C incorporated in the neopentane liberated during grafting (%Np*) and the percentage of ^{13}C labeling on each of the ligands in **1c** (P_x*). For pathway (i), every alkyl ligand has an equiprobability to be transformed into neopentane; hence the probability to observe labeled neopentane (P_1) is equal to the percentage of labeling of the alkyl moiety (P_{alkyl}*). For pathway (ii), the probability of observing labeled neopentane (P_2; eq 3) depends for $^2/_3$ on the percentage of labeling of the alkyl moiety (P_{alkyl}*) and for $^1/_3$ on the percentage of labeling of the alkylidene moiety ($P_{alkylidene}$*).

$$\text{fraction of pathway (i)} = \frac{(\%\text{Np*}/100) - P_2}{P_1 - P_2} \qquad (1)$$

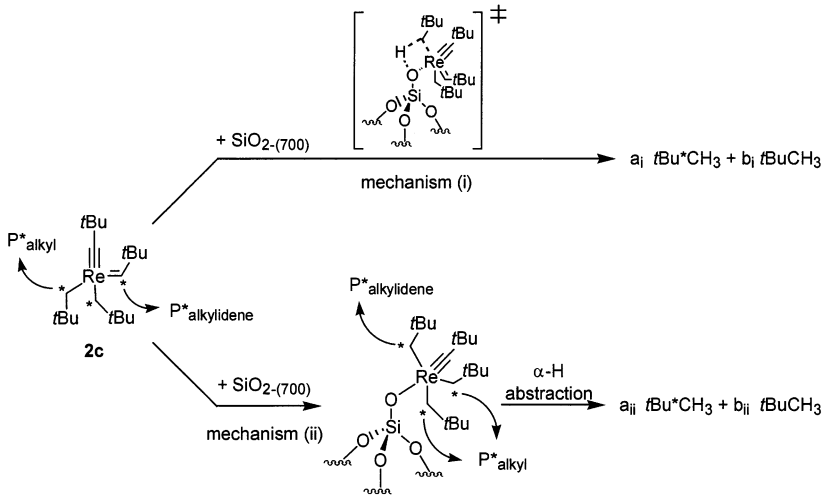
$$\text{fraction of pathway (ii)} = 1 - (\text{fraction of pathway (i)}) \qquad (2)$$

with

$$P_1 = P_{alkyl}* \quad \text{and} \quad P_2 = \frac{2}{3} \times P_{alkyl}* + \frac{1}{3} \times P_{alkylidene}* \qquad (3)$$

The grafting of **1c** onto $SiO_{2-(700)}$ yielded neopentane 81 ± 5% ^{13}C-labeled according to mass spectroscopy. Therefore, applying this model to the experimental results suggests that 57 ± 20% of grafting would occur via mechanism (i) and the remaining amount (43 ± 20%) occurs via mechanism (ii).

Scheme 9. Isotopic Distribution of Neopentane Released During the Grafting of **1c** onto $SiO_{2-(700)}$, Following Either Pathway (i) or Pathway (ii)



Moreover, these reaction pathways are usually estimated from the reaction of the organometallic complex and deuterated silica readily obtained from H/D exchange with D_2O. Therefore, the grafting of **1a** was performed on a 92% deuterated silica. Because the addition of (≡SiO−H) onto the carbynic moiety has been ruled out, the relative contribution of pathways (i) and (ii) can be determined by quantifying monodeuterated and nondeuterated neopentane released during the grafting of **1a** onto partially deuterated $SiO_{2-(700)}$ (eqs 4 and 5).

Moreover, because the deuteration of $SiO_{2-(700)}$ is usually only partial (typically 90−95%), the model must integrate the percentage of nondeuterated silanol groups (%SiOH) present on the partially deuterated $SiO_{2-(700)}$. The reaction of **1a** with ≡SiOH produces indeed only nondeuterated neopentane whatever the pathway is. With all of these facts in hand, it is possible to obtain the fraction of the pathways (i) and (ii) depending on the percentage of deuteration in neopentane liberated in the gas phase (%NpD, eqs 4−6). The probability for the elimination of monodeuterated neopentane (P_1) in pathway (i) is equal to 1 in any case, while the probability for the elimination of monodeuterated neopentane (P_2) in pathway (ii) is $^1/_2$ if isotope effects in the α−H abstraction step are considered negligible. If isotope effects (k_H/k_D) are taken into account, P_2 can easily be estimated (eq 6 and vide infra for comments).

$$\text{fraction of pathway (i)} = \frac{\%\text{NpD} - P_2 \times (100 - \%\text{SiOH})}{(100 - \%\text{SiOH}) \times (P_1 - P_2)} \quad (4)$$

$$\text{fraction of pathway (ii)} = 1 - (\text{fraction of pathway (i)}) \quad (5)$$

with

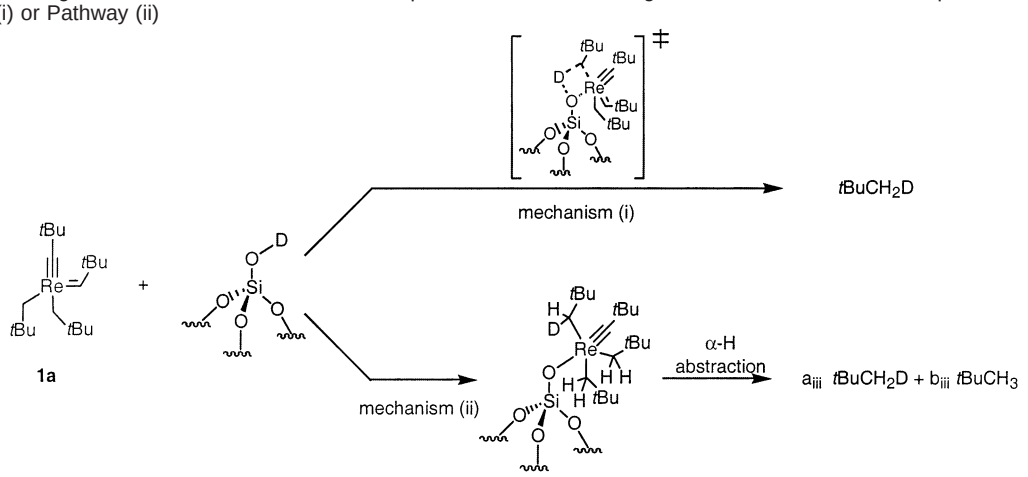
$$P_1 = 1 \quad \text{and} \quad P_2 = \frac{(k_H/k_D) + 1}{3\,(k_H/k_D) + 1} \qquad (P_2 = 0.5 \text{ for } k_H/k_D = 1) \quad (6)$$

The grafting of **1a** onto 92% deuterated $SiO_{2-(700)}$ yielded neopentane on average 74 ± 5% monodeuterated and 26 ± 5% nondeuterated according to mass spectroscopy. A simple electrophilic cleavage of a Re−alkyl bond by a surface SiO−D bond (mechanism (i)) would produce monodeuterated neopentane as the sole isotopomer, that is, a mixture 92/8 of mono- and nondeuterated neopentane on 92% deuterated silica. The formation of 26% of nondeuterated neopentane shows that the grafting has to also involve the addition of the silanol on the alkylidene moieties of **1a** followed by an α-abstraction (vide supra mechanism (ii)). Applying this model to our experimental results (%SiOH = 8%, %NpD = 74 ± 5%, and %NpH = 26 ± 5%, $k_H/k_D = 1$) shows that grafting occurs 61 ± 10% via mechanism (i) and 39 ± 10% via mechanism (ii) (Scheme 9), which is to be compared with the results obtained from the experiment using ^{13}C-labeled **1c** and which shows that grafting occurs 57 ± 20% via mechanism (i) and 43 ± 20% via mechanism (ii). Noteworthy is the good agreement between these two independent methods to determine the relative contribution of mechanisms (i) and (ii). Moreover, looking into the influence of isotope effects on the relative distribution of mono- and nondeuterated neopentane shows that they have little effect on the determination of each pathway (it falls within experimental errors, which preclude, in turn, their evaluation).[18] In conclusion, about 60 ± 10% of **1a** reacts with $SiO_{2-(700)}$ via mechanism (i), while 40 ± 10% reacts via mechanism (ii) (Scheme 10). Because **1a** contains two alkyl ligands for one alkylidene ligand, the reactivity ratio between alkylidene and alkyl ligands is 1.3 ± 0.6, showing that, in this case, alkyl and alkylidene moieties have in fact a similar reactivity toward silanols.

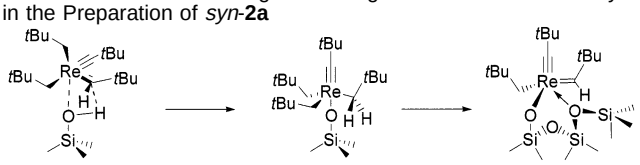
These data are in sharp contrast to what has been observed in molecular chemistry because the reaction of **1a** with Brönsted acids (HX, X = Cl, OC_6F_5, BF_4, OTf, etc.) gives the products resulting exclusively from the protonation onto the alkylidene moiety, [Re(≡C^{t}Bu)($CH_2{}^t$Bu)$_3$X], which can be isolated in fairly good yields (60−80%).[1b] These compounds do not undergo spontaneously α-H abstraction of neopentane to give alkylidene complexes. This α-H abstraction step has to be induced by adding donor ligands such as pyridine, acetonitrile, or methanol. By comparison, the reaction of **1a** with silica would proceed via both addition of ≡SiO−H to the carbenic moiety, giving [(≡SiO)−Re(≡C^{t}Bu)($CH_2{}^t$Bu)$_3$] as a transient state, and direct electrophilic cleavage of the Re−$CH_2{}^t$Bu bond, both leading to *syn*-**2a** without addition of an external molecular ligand. The

(18) For example, using a k_H/k_D of 2 and 7 would lead to our case of F(i) equal to 66 and 69%, respectively, to be compared with 61% assuming no isotope effect.

Scheme 10. Percentage of Non- and Monodeuterated Neopentane Produced During the Reaction of ≡SiOD Groups with **1a** Following Either Pathway (i) or Pathway (ii)



Scheme 11. Understanding of the Origin of the Stereoselectivity in the Preparation of *syn*-**2a**



EXAFS data point out the presence of a siloxane bridge (donor ligand) in the coordination of **2a**, which could have played the role of the external ligand to induce the spontaneous extrusion of the neopentyl ligand in [(≡SiO)−Re(≡C*t*Bu)(CH_2*t*Bu)$_3$] to form directly **2a**. Another possibility would conciliate the observation in molecular (sole reactivity of the alkylidene ligand) and surface organometallic chemistry, that is, if the addition of the silanol onto the carbene would be reversible. Indeed, in this case, successive addition and its reverse reaction would lead to scrambling of the labels (^{2}H or ^{13}C), which would therefore preclude the possibility to evaluate the proportion of pathway (i) because pathway (ii) would have a similar effect on the isotopomer distribution. Therefore, the surface reaction could well-occur completely via pathway (ii) if the addition of the silanol onto the carbene is reversible. It is, however, difficult to probe this mechanism.

Finally, as a molecular chemist, one might ask why **2a** is obtained as a single isomer. The molecular complex **1a** is present as a single isomer, probably the syn rotamer according to NMR data. While the direct electrophilic cleavage should provide *syn*-**2a** in any case, the process involving the addition to the carbenic moiety has to be stereoselective. The addition of the silanol involves first its coordination to the Re center to form probably a distorted trigonal bipyramidal surface complex[19] (Scheme 11), followed by the addition of the proton to the carbenic moiety, while the *t*Bu group points away from the surface. The subsequent α-H abstraction step thus generates *syn*-**2a**.

Conclusion

The reaction of **1a** with silica dehydroxylated at 700 °C has been investigated by IR, elemental analysis, chemical reactivity, EXAFS, 1D and 2D solid-state NMR spectroscopy, and synthesis of molecular models. The data are fully consistent with the formation of only one surface species **2a**, grafted to the surface via one SiO−Re linkage and containing a neopentyl, a neopentylidene, and a neopentylidyne ligand along with a siloxane bridge, ([(≡SiO)−Re(≡C*t*Bu)(═CH*t*Bu)(CH_2*t*Bu)-(≡SiOSi≡)]). This surface complex was found to be present only as its syn rotamer (*syn*-**2a**). The grafting probably proceeds via two pathways: direct protolytic cleavage of a Re−neopentyl bond of **1a** by SiO−H (60%) and addition of SiO−H bond onto the alkylidene moiety of **1a** followed by α-H abstraction (40%). The neopentylidyne ligand of **1a** has been found unreactive under these conditions and acts as a spectator ligand during the grafting. Interestingly, *syn*-**2a** can be partially isomerized into its anti rotamer (*anti*-**2**) either by heating or by exposing it to light. This study further demonstrates that surface organometallic chemistry can allow the preparation of well-defined surface organometallic species, which can be characterized at a molecular level. Finally, like Schrock et al. stated in 1983,[1a] "[Re(≡C*t*Bu)(═CH*t*Bu)(CH_2*t*Bu)$_2$] is an especially interesting species in the sense it fills out the series of four-coordinate compounds...," we would like to make the same comment concerning **2a**, [(≡SiO)Re(≡C*t*Bu)(═CH*t*Bu)(CH_2*t*Bu)$_2$], in view of the recently characterized corresponding surface complexes of Ta,[5b] Mo,[5a] and W[20] as [(≡SiO)Ta(═CH*t*Bu)-(CH_2*t*Bu)$_2$] and [(≡SiO)M(≡C*t*Bu)(CH_2*t*Bu)$_2$] for M = Mo and W.

Experimental Section

All experiments were carried out in the strict absence of oxygen and water. Standard Schlenk techniques under argon were used for organometallic syntheses. Surface compounds were dried under high vacuum (10^{-5} Torr). Pentane, dichloromethane, diethyl ether, and THF were purified according to the published procedures.[21] C_6D_6 (SDS) was distilled over Na/benzophenone and stored over 3 Å molecular sieves. [Re(═N*t*Bu)$_2$Cl$_3$] was prepared in a one-pot reaction involving Re_2O_7 (99.9%, Strem Chemicals), *t*BuNH$_2$ (99.5%, Aldrich), $(CH_3)_3SiCl$ (99%, Aldrich), and anhydrous gaseous HCl (Air Liquide), used as received, following a literature procedure.[1] 2,4-Lutidine hydrochloride was prepared by bubbling an excess of anhydrous gaseous HCl into a solution of 2,4-lutidine (98%, Acros) in diethyl ether, followed by filtration and washing steps. Ph_3SiOH (Aldrich) and the polyoligomeric silsesquioxane **3** (Aldrich) were dried under high vacuum prior use, at 25 °C (4 h) and at 40 °C (12 h), respectively. SiO_2 (Aerosil Degussa, 200 m^2/g) was calcined at 400 °C in air for 2 h, partially dehydroxylated

(19) Schrock, R. R.; Crowe, W. E.; Bazan, G. C.; DiMare, M.; O'Regan, M. B.; Schofield, M. H. *Organometallics* **1991**, *10*, 1832. See also ref 1b.

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at 500 °C under high vacuum (10^{-5} mmHg) for 12 h, and then at 700 °C for 4 h (support referred to as $SiO_{2-(700)}$). In experiments requiring deuterated silica, a similar procedure was used, but the first partial dehydroxylation at 500 °C was followed by D_2O treatment and partial dehydroxylation at 500 °C for 5 h (five cycles). After partial dehydroxylation at 700 °C for 4 h, silica was 92−93% deuterated according to IR spectroscopy. Solution NMR spectroscopy was recorded on a Bruker ACX-300 and DRX-500 spectrometer. ^{1}H NMR spectra were referenced to C_6D_5H at 7.15 ppm. ^{13}C NMR spectra were referenced to C_6D_6 at 128.0 ppm. GC analysis of neopentane was performed on a gas chromatograph HP 5890, equipped with a flame ionization detector (FID) and a KCl/Al_2O_3 on fused silica column (50 m × 0.32 mm). 1D MAS ^{1}H and ^{13}C CP/MAS solid-state NMR spectra were recorded on a Bruker DSX-300 spectrometer operating at 300 and 75 MHz for ^{1}H and ^{13}C, respectively. The samples were introduced under Ar in a zirconia rotor, which was then tightly closed. In all experiments, the sample rotation frequency was set to 10 kHz. Chemical shifts are given with respect to TMS as an external standard, with a precision of 0.2 and 1 ppm for ^{1}H and ^{13}C NMR, respectively. For CP/MAS ^{13}C NMR, the following sequence was used: 90° pulse on the protons (pulse length 3.8 μs), then a cross-polarization step with a contact time typically set to 5 or 10 ms, and finally acquisition of the ^{13}C signal under high power proton decoupling. The delay between each scan was set to 1 s, to allow the complete relaxation of the ^{1}H nuclei. For direct excitation ^{13}C NMR, the following sequence was used: pulse on the carbons (impulsion length 3.0 μs) and recording of the ^{13}C signal under high power proton decoupling. The delay between each scan was set to 1 s. For both CP/MAS and direct excitation ^{13}C NMR, an apodization function (exponential) corresponding to a line-broadening of 50 Hz was applied. The 2D solid-state NMR spectroscopy experiments were conducted on a Bruker DSX 500 spectrometer using a 4-mm MAS probe. For the cross-polarization step, a ramped radio frequency (RF) field centered at 77 kHz was applied to protons, while the carbon RF field was matched to obtain optimal signal. During acquisition, the proton decoupling field strength was also set to 77 kHz. A total of 64 t_1 increments with 256 scans each were collected. The sample spinning frequency was 10 kHz, and the contact time for the cross-polarization step was set to a value as defined in the figures. Quadrature detection in ω_1 was achieved using the TPPI method.[22] For EXAFS experiments, the samples were packaged in aluminum holders with Kapton tape and sealed inside two Mylar pouches in an Ar filled drybox. The samples were then put into glass jars and sealed with Teflon tape inside the drybox. Everything except for the Teflon tape was baked out at 110 °C overnight. X-ray absorption spectra were acquired at the Stanford Synchrotron Radiation Laboratory (SSRL) at beam-line 4-1 using a $Si_{(220)}$ double crystal monochromator detuned 50% to reduce the higher order harmonic content of the beam. X-ray absorption spectra were obtained in the transmission mode at room temperature using argon filled ionization chambers. The data analysis was performed by standard procedures using the EXAFSPAK suite of programs developed by G. George of SSRL.[23] Fitting of the spectrum was done on the k^3-weighted data using the following EXAFS equation where S_0^2 is the scale factor, fixed at 0.9; N_i is the coordination number of shell i; S_i is the central atom loss factor for atom i; F_i is the EXAFS scattering function for atom i; R_i is the distance to atom i from the absorbing atom; λ_i is the photoelectron mean free path; σ_i is the Debye−Waller factor; ϕ_i is the EXAFS phase function for atom i; and ϕ_c is the EXAFS phase function for the absorbing atom.

$$\chi(k) \cong S_0^2 \sum_{i=1}^{n} \frac{N_i S_i(k,R_i) F_i(k,R_i)}{kR_i^2} \exp\left(\frac{-2R_i}{\lambda(k,R_i)}\right) \exp(-2\sigma_i^2 k_i^2) \sin[2kR_i + \phi_i(k,R_i) + \phi_c(k)]$$

The program FEFF8[24] was used to calculate theoretical values for S_i, F_i, λ_i, ϕ_i, and ϕ_c on the basis of atomic positions taken from the crystal structure of the most similar complex.

Synthesis of 1a. The rhenium complex **1a** was prepared in four steps according to a literature procedure[1a] starting from Re_2O_7 and involving the following intermediates: [Re(=N^{t}Bu)$_2$Cl$_3$],[1b] [Re(=N^{t}Bu)$_2$(=CH-^{t}Bu)(CH$_2$^{t}Bu)],[1a] and [Re(≡C^{t}Bu)(=CH^{t}Bu)−(NH$_2$^{t}Bu)Cl$_2$]$_2$·(THF).[1a] Overall yields were in the range 30−40% (lit. 45%). ^{1}H NMR (C_6D_6): δ 1.10 (s, 18H, C**H**$_3$), 1.27 (s, 9H, C**H**$_3$), 1.38 (s, 9H, C**H**$_3$), 1.55 (d, $^2J_{HaHb}$ = 12.3 Hz, 2H, ReC**H**$_a$H$_b$^{t}Bu), 1.89 (d, $^2J_{HaHb}$ = 12.3 Hz, 2H, ReCH$_a$**H**$_b$^{t}Bu), 7.65 (s, 1H, Re=C**H**^{t}Bu) ppm. ^{13}C NMR ($CDCl_3$): δ 29.7 (CC(C**H**$_3$)$_3$), 32.4 (CC(C**H**$_3$)$_3$), 34.6 (CC(C**H**$_3$)$_3$), 35.1 (ReCH$_2$-**C**(CH$_3$)$_3$), 43.1 (Re=CH**C**(CH$_3$)$_3$), 52.6 (Re≡C**C**(CH$_3$)$_3$), 78.6 (Re**C**H$_2$-^{t}Bu), 224.4 (Re=C**H**^{t}Bu), 295.1 (Re≡**C**^{t}Bu) ppm.

Preparation of Labeled 1b−e. (1-^{13}C, 99%) Monolabeled neopentylmagnesium chloride was prepared in four steps starting from ^{13}C-labeled (carbonyl, 1-^{13}C, 99%) dimethylformamide (H^{13}CONMe$_2$, DMF*), using the following sequence: reaction of ^{t}BuLi with DMF* to form (1-^{13}C, 99%) 2,2-dimethylpropanal (not isolated), followed by a reduction with $LiAlH_4$ to yield the corresponding alcohol (step 1), a tosylation (step 2), and a nucleophilic substitution with LiCl to give ^{13}C-monolabeled (1-^{13}C, 99%) 2,2-dimethylchloropropane (step 3). It was then transformed into the corresponding Grignard reagent (step 4).

Step 1: Synthesis of ^{t}Bu^{13}CH$_2$OH. To a mixture of DMF* (6.9 g, 93.2 mmol) and diethyl ether (200 mL) at −78 °C was added ^{t}BuLi (1.7 M solution in pentane, 73 mL, 124 mmol) in 30 min under vigorous stirring. The light yellow resulting reaction mixture was allowed to warm to 25 °C, stirred for 30 min, and transferred via a cannula into 200 mL of a 3 M aqueous solution of HCl. The aqueous phase was extracted with diethyl ether. The combined organic layers were washed with a saturated aqueous solution of $NaHCO_3$ and dried 30 min over $MgSO_4$. The resulting solution was treated by $LiAlH_4$ (2.7 g, 71.1 mmol), stirred for 15 min, and treated with a saturated aqueous solution of Na_2SO_4. The aqueous phase was extracted with diethyl ether, and the combined organic phases were dried over $MgSO_4$. After evaporation of diethyl ether under atmospheric pressure, a colorless oil (7.43 g, 89.5%) was obtained. ^{1}H NMR (C_6D_6): δ 0.81 (d, $^3J_{CH}$ = 4.8 Hz, 9H, (C**H**$_3$)$_3$C^{13}CH$_2$OH), 0.96 (br, 1H, ^{t}Bu^{13}CH$_2$O**H**), 3.03 (d, $^1J_{CH}$ = 140 Hz, 2H, ^{t}Bu^{13}C**H**$_2$OH) ppm.

Step 2: Synthesis of ^{t}Bu^{13}CH$_2$OTs. *p*-Toluenesulfonyl chloride (16.7 g, 87.7 mmol) was slowly added to a solution containing ^{t}BuCH$_2$OH (7.43 g, 83.5 mmol), pyridine (13.4 mL, 166 mmol), and CH_2Cl_2 (85 mL). The reaction mixture was stirred at room temperature for 2 days and then treated by 130 mL of a 1.5 M HCl aqueous solution. The aqueous phase was extracted four times with CH_2Cl_2 (20 mL). The combined organic phases were washed with a saturated aqueous solution of $NaHCO_3$ (40 mL), dried 30 min over $MgSO_4$, and evaporated to give a colorless oil (19.0 g, 93.5%), which crystallized after 24 h at room temperature. ^{1}H NMR ($CDCl_3$): δ 0.88 (d, $^3J_{CH}$ = 4.7 Hz, 9H, (C**H**$_3$)$_3$C^{13}CH$_2$OTs), 2.44 (s, 3H, C**H**$_3$−Ar), 3.64 (d, $^1J_{CH}$ = 148 Hz, 2H, ^{t}Bu^{13}C**H**$_2$OTs), 7.33 (d, $^3J_{HH}$ = 8.3 Hz, 2H, Ar), 7.77 (d, $^3J_{HH}$ = 8.3 Hz, 2H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ 21.6 (**C**H$_3$−Ar), 26.0 ((**C**H$_3$)$_3$C^{13}CH$_2$OTs), 31.6 ((CH$_3$)$_3$**C**^{13}CH$_2$OTs), 79.5 (^{t}Bu**^{13}C**H$_2$OTs), 127.9 (Ar), 129.7 (Ar), 133.0 (Ar), 144.6 (Ar) ppm.

Step 3: Synthesis of ^{t}Bu^{13}CH$_2$Cl. To a 100 mL round-bottom flask equipped with a short path distillation apparatus and a receiver Schlenk were added under argon ^{t}Bu^{13}CH$_2$OTs (19.0 g, 78.2 mmol), DMPU (1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidone, 35 mL), and anhydrous LiCl (9.2 g, 217 mmol). The mixture was heated to 130 °C under vigorous stirring, and ^{t}Bu^{13}CH$_2$Cl (7.4 g, 88%) slowly distilled off in 16 h. ^{1}H NMR (C_6D_6): δ 0.77 (d, $^3J_{CH}$ = 5.3 Hz, 9H, (C**H**$_3$)$_3$C^{13}-CH$_2$Cl), 2.95 (d, $^1J_{CH}$ = 148.3 Hz, 2H, ^{t}Bu^{13}C**H**$_2$Cl) ppm. ^{13}C NMR

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($CDCl_3$): δ 27.1 (($\mathbf{C}H_3)_3C^{13}CH_2Cl$), 33.1 (($CH_3)_3\mathbf{C}^{13}CH_2Cl$), 57.3 (^{t}Bu$^{\mathbf{13}}\mathbf{C}H_2Cl$) ppm.

Step 4: Synthesis of ^{t}Bu^{13}CH$_2$MgCl. Turnings of Mg (1.6 g, 65.8 mmol) were activated at 400 °C under vacuum. A solution of ^{t}Bu$^{13}CH_2Cl$ (6.8 mL; 54.8 mmol) in diethyl ether (10 mL) and THF (10 mL) was then added under argon, heated to reflux, treated with 0.1 mL of 1,2-dibromoethane, and then heated at 110 °C overnight. The resulting mixture was then filtered, and the filtrate was diluted with diethyl ether (30 mL). A 0.87 M solution of ^{t}Bu$^{13}CH_2MgCl$ in diethyl ether/THF was obtained (42 mL, 66.7%).

Synthesis of 1b. This complex, 10% randomly ^{13}C-labeled on the α-carbons, can be prepared in a manner similar to that of **1a**, by using a 90/10 mixture of nonlabeled and 100% ^{13}C-labeled neopentylmagnesium chloride as alkylating agent in the two alkylation steps.

Synthesis of [Re(≡^{13}C^{t}Bu)(=^{13}CH^{t}Bu)(^{13}CH$_2{}^t$Bu)$_2$], 2b. This compound was prepared in a three-step procedure starting from [Re(=N-^{t}Bu)$_2$Cl$_3$], via the intermediates [Re(=N^{t}Bu)$_2$(=^{13}CH^{t}Bu)(^{13}CH$_2{}^t$Bu)] and [Re(≡^{13}C^{t}Bu)(=^{13}CH^{t}Bu)(NH$_2{}^t$Bu)Cl$_2$]$_2$·(THF).

Step 1: Synthesis of [Re(=N^{t}Bu)$_2$(=^{13}CH^{t}Bu)(^{13}CH$_2{}^t$Bu)]. To a solution of [Re(=N^{t}Bu)$_2$Cl$_3$] (1.3 g, 2.99 mmol) in diethyl ether (50 mL) was added dropwise at −78 °C a 0.87 M solution of ^{t}Bu^{13}CH$_2$-MgCl in diethyl ether/THF (10.3 mL, 8.97 mmol). The resulting deep purple solution was allowed to warm to room temperature, and the color turned to brown-green. The reaction mixture was stirred at room temperature for 2 h, filtered through Celite, and the filtrate was evaporated to dryness to give a dark residue. Sublimation under vacuum (10^{-5} Torr) at 80 °C gave a yellow oil (0.83 g, 59%). ^{1}H NMR (C_6D_6): δ 1.19 (d, $^3J_{CH}$ = 4.8 Hz, 9H, C$\mathbf{H}_3$), 1.29 (d, $^3J_{CH}$ = 4.8 Hz, 9H, C$\mathbf{H}_3$), 1.37 (s, 18H, =N^{t}Bu), 2.69 (dd, $^2J_{HaHb}$ = 13.3 Hz, $^1J_{CHa}$ = 126 Hz, 2H, ReC$\mathbf{H_a}$H$_b{}^t$Bu), 2.90 (dd, $^2J_{HaHb}$ = 13.3 Hz, $^1J_{CHb}$ = 126 Hz, 2H, ReCH$_a\mathbf{H_b}{}^t$Bu), 12.02 (d, $^1J_{CH}$ = 133 Hz, 1H, Re=C$\mathbf{H}{}^t$Bu) ppm. ^{13}C NMR (C_6D_6) labeled carbons: δ 34.5 (Re$\mathbf{C}H_2{}^t$Bu), 262.4 (Re=$\mathbf{C}$H-^{t}Bu) ppm.

Step 2: Synthesis of [Re(≡^{13}C^{t}Bu)(=^{13}CH^{t}Bu)(NH$_2{}^t$Bu)Cl$_2$]$_2$·(THF).[4b] 2,4-Lutidine hydrochloride (0.62 g, 4.31 mmol) was added to a solution of [Re(=N^{t}Bu)$_2$(=^{13}CH^{t}Bu)(^{13}CH$_2{}^t$Bu)] (0.67 g, 1.42 mmol) in CH_2Cl_2 cooled at −40 °C. The color changed from yellow to orange. The mixture was stirred at −40 °C for 1.5 h and then at 0 °C for 1 h. The white powder of ^{t}BuNH$_3$Cl was removed by filtration through Celite and carefully extracted with 3 × 2 mL of CH_2Cl_2. The combined fractions were evaporated in vacuo to give a light orange powder (0.63 g, 87%) which can be crystallized from a 1:1 mixture of THF and pentane at −40 °C. ^{1}H NMR ($CDCl_3$): major isomer δ 1.18 (s, 18 H, ($\mathbf{C}H_3)_3CNH_2$), 1.30 (d, $^3J_{CH}$ = 4.4 Hz, 18H, C$\mathbf{H}_3$), 1.40 (d, $^3J_{CH}$ = 4.4 Hz, 18H, C$\mathbf{H}_3$), 1.84 (m, THF), 3.72 (m, THF), 4.25 (d, $^2J_{HaHb}$ = 12.5 Hz, 2H, ^{t}BuN$\mathbf{H_a}$H$_b$), 5.34 (d, $^2J_{HaHb}$ = 13.0 Hz, 2H, ^{t}BuNH$_a\mathbf{H_b}$), 13.64 (dd, $^1J_{CH}$ = 123.3 Hz, $^3J_{HCReC}$ = 3.4 Hz, 2H, Re=C$\mathbf{H}{}^t$Bu); minor isomer δ 1.19 (s, 18 H, ($\mathbf{C}H_3)_3CNH_2$), 1.29 (d, $^3J_{CH}$ = 5.5 Hz, 18H, C$\mathbf{H}_3$), 1.41 (d, $^3J_{CH}$ = 4.0 Hz, 18H, C$\mathbf{H}_3$), 1.84 (m, THF), 3.72 (m, THF), 4.39 (d, $^2J_{HaHb}$ = 12.5 Hz, 2H, ^{t}BuN$\mathbf{H_a}$H$_b$), 5.13 (d, $^2J_{HaHb}$ = 13.0 Hz, 2H, ^{t}BuNH$_a\mathbf{H_b}$), 13.59 (dd, $^1J_{CH}$ = 123.8 Hz, $^3J_{HCReC}$ = 3.6 Hz, 2H, Re=C$\mathbf{H}{}^t$Bu) ppm.^{13}C NMR ($CDCl_3$) labeled carbons: major isomer δ 294.6 (d, $^2J_{CReC}$ = 6.6 Hz, Re≡$\mathbf{C}{}^t$Bu), 298.7 (d, $^2J_{CReC}$ = 6.6 Hz, $^1J_{CH}$ = 123 Hz, Re=$\mathbf{C}$H^{t}Bu); minor isomer δ 294.0 (d, $^2J_{CReC}$ = 6.6 Hz, Re≡$\mathbf{C}{}^t$Bu), 299.5 (d, $^2J_{CReC}$ = 6.6 Hz, $^1J_{CH}$ = 124 Hz, Re=$\mathbf{C}$H^{t}Bu) ppm.

Step 3: Conversion of 4b [Re(≡^{13}C^{t}Bu)(=^{13}CH^{t}Bu)(NH$_2{}^t$Bu)Cl$_2$]$_2$·(THF) into 1c. A solution of **4b** (0.15 g, 0.15 mmol) in THF (5 mL) was cooled to −40 °C, and a 0.87 M solution of ^{t}Bu^{13}CH$_2$MgCl in diethyl ether/THF (0.7 mL, 0.61 mmol) was added dropwise. The mixture was stirred for 45 min at −40 °C, and the solvent was then evaporated. The residue was extracted with pentane (15 mL). The extract was filtered through Celite and evaporated in vacuo to give a yellow-orange oil, which can be purified by sublimation at room temperature under vacuum (10^{-5} Torr) onto a coldfinger (liquid N_2). ^{1}H NMR (C_6D_6): δ 1.11 (d, $^3J_{CH}$ = 4.8 Hz, 18H, C$\mathbf{H}_3$), 1.27 (d, $^3J_{CH}$ = 4.8 Hz, 9H, C$\mathbf{H}_3$), 1.38 (d, $^3J_{CH}$ = 4.7 Hz, 9H, C$\mathbf{H}_3$), 1.89 (dd, $^1J_{CH}$ = 116 Hz, $^2J_{HaHb}$ = 13 Hz, 2H, Re^{13}C$\mathbf{H_a}$H$_b{}^t$Bu), 7.65 (dd, $^1J_{CH}$ = 115 Hz, $^3J_{HCReC}$ = 5.3 Hz, 1H, Re=^{13}C$\mathbf{H}{}^t$Bu) ppm. ^{13}C NMR ($CDCl_3$) labeled carbons: δ 78.6 (Re$\mathbf{C}H_2{}^t$Bu), 224.4 (Re=$\mathbf{C}$H^{t}Bu), 295.1 (Re≡$\mathbf{C}{}^t$Bu) ppm.

Synthesis of 1d. A solution of [Re(≡C^{t}Bu)(=CH^{t}Bu)(NH$_2{}^t$Bu)Cl$_2$]$_2$·(THF) (0.32 g, 0.31 mmol) in THF (10 mL) was cooled to −40 °C, and a 0.87 M solution of ^{t}Bu^{13}CH$_2$MgCl in diethyl ether/THF (1.6 mL, 1.39 mmol) was added dropwise. The mixture was stirred for 45 min at −40 °C, and the solvent was then evaporated. The residue was extracted with pentane (15 mL). The extract was filtered through Celite, and the solvent was removed from the filtrate in vacuo, leaving a yellow-orange oil which can be purified by sublimation at room temperature under vacuum (10^{-5} Torr) onto a coldfinger (liquid N_2). ^{1}H NMR (C_6D_6): δ 1.11 (d, $^3J_{CH}$ = 4.8 Hz, 18H, C$\mathbf{H}_3$), 1.27 (d, $^3J_{CH}$ = 4.8 Hz, 9H, C$\mathbf{H}_3$), 1.38 (d, $^3J_{CH}$ = 4.7 Hz, 9H, C$\mathbf{H}_3$), 7.65 (dd, $^1J_{CH}$ = 115 Hz, $^3J_{HCReC}$ = 5.3 Hz, 1H, Re=^{13}C$\mathbf{H}{}^t$Bu) ppm. ^{13}C NMR ($CDCl_3$) labeled carbons: δ 78.6 (Re$\mathbf{C}H_2{}^t$Bu), 224.4 (Re=$\mathbf{C}$H^{t}Bu), 295.1 (Re≡$\mathbf{C}{}^t$Bu) ppm.

Synthesis of 1e. A solution of **4b** [Re(≡^{13}C^{t}Bu)(=^{13}CH^{t}Bu)(NH$_2$-^{t}Bu)Cl$_2$]$_2$·(THF) (0.30 g, 0.30 mmol) in THF (10 mL) was cooled to −40 °C, and a 0.87 M solution of ^{t}Bu^{13}CH$_2$MgCl in diethyl ether/THF (1.32 mmol) was added dropwise. The mixture was stirred for 45 min at −40 °C, and the solvent was then evaporated. The residue was extracted with pentane (15 mL). The extract was filtered through Celite, and the solvent was removed from the filtrate in vacuo, leaving a yellow-orange oil which can be purified by sublimation at room temperature under vacuum (10^{-5} Torr) onto a coldfinger (liquid N_2). ^{1}H NMR (C_6D_6): δ 1.11 (d, $^3J_{CH}$ = 4.8 Hz, 18H, C$\mathbf{H}_3$), 1.27 (d, $^3J_{CH}$ = 4.8 Hz, 9H, C$\mathbf{H}_3$), 1.38 (d, $^3J_{CH}$ = 4.7 Hz, 9H, C$\mathbf{H}_3$), 7.65 (dd, $^1J_{CH}$ = 115 Hz, $^3J_{HCReC}$ = 5.3 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$) labeled carbons: δ 78.6 (Re$\mathbf{C}H_2{}^t$Bu), 224.4 (Re=$\mathbf{C}$H^{t}Bu), 295.1 (Re≡$\mathbf{C}{}^t$Bu) ppm.

Synthesis of 2a by Impregnation of 1a onto $SiO_{2-(700)}$. A mixture of **1a** (200 mg, 0.43 mmol) and $SiO_{2-(700)}$ (1.00 g) in pentane (10 mL) was stirred at 20 °C for 2 h. After being filtered, the solid was washed three times with pentane, and all volatile compounds were condensed into another reactor of known volume to quantify neopentane evolved during the grafting. The resulting yellow powder was dried under vacuum (10^{-5} Torr) to yield 1.1 g of **2a**. Analysis by gas chromatrography indicated the formation of 0.24 mmol of neopentane during grafting. Elemental analysis of **1a**: C, 4.55%$_w$ and Re, 4.75%$_w$ (found, C/Re = 14.86; calcd for **1a**, C/Re = 15.00). Solid-state MAS ^{1}H NMR (300 MHz): δ 1.2, 2.6, 3.0, and 11.1 ppm. CP/MAS ^{13}C NMR: δ 30.3, 44.4, and 245.8 (weak) ppm. IR: 2960, 2932, 2905, 2873, 2742, 1474, 1461, 1390, 1363 cm^{-1}. ESR: no signal.

Synthesis of 2a by Impregnation of 1a onto Deuterated $SiO_{2-(700)}$. A similar procedure was used in which SiO_{2-700} was replaced by deuterated $SiO_{2-(700)}$. Analysis of the evolved neopentane by GC/MS gave reproducibly the following isotopomeric composition: d_0-neopentane (26 ± 5%), d_1-neopentane (74 ± 5%), d_2 and other isotopomers (traces < 1%).

Synthesis of 2b by Impregnation of 1b onto $SiO_{2-(700)}$. The surface compound **2b** was prepared in a manner similar to that of **2a**, using **1b** in place of **1a**. Solid-state MAS ^{1}H NMR (500 MHz): δ 1.1, 1.3, 1.5, 2.6, 3.1, and 11.1 ppm. CP/MAS ^{13}C NMR: δ 29, 46, and 247 ppm. Direct excitation ^{13}C NMR: δ 30, 44, 246, and 292 ppm.

Synthesis of 2c by Impregnation of 1c onto $SiO_{2-(700)}$. Compound **2c** was prepared in a manner similar to that of **2a**, using **1c** in place of **1a**. Solid-state MAS ^{1}H NMR (300 MHz): δ 1.1 and 10.8 ppm. CP/MAS ^{13}C NMR: δ 31, 46, and 246 ppm. Direct excitation ^{13}C NMR: δ 31, 45, and 247 ppm. No carbynic signal observed.

Synthesis of 2d by Impregnation of 1d onto $SiO_{2-(700)}$. Compound **2d** was prepared in a manner similar to that of **2a**, using **1d** in place of **1a**. Solid-state MAS ^{1}H NMR (300 MHz): δ 1.1 and 10.9 ppm.

CP/MAS ^{13}C NMR: δ 30, 45, 246, and 292 ppm. Direct excitation ^{13}C NMR: δ 30, 47, 247, and 293 ppm.

Synthesis of 2e by Impregnation of 1e onto $SiO_{2-(700)}$. Compound **2e** was prepared in a manner similar to that of **2a**, using **1e** in place of **1a**. Solid-state MAS ^{1}H NMR (300 MHz): δ 1.0 and 11.0 ppm. CP/MAS ^{13}C NMR: δ 31, 47, 247, and 294 ppm. Direct excitation ^{13}C NMR: δ 32, 47, 248, and 294 ppm.

Hydrogenolysis of the Surface Complex 2a. First 20−40 mg of silica was pressed into a 18 mm self-supporting disk, put into a sealed glass high-vacuum reactor equipped with CaF_2 windows, and partially dehydroxylated under vacuum (500 °C, 12 h and 700 °C, 4 h). Compound **1a** was then sublimed under dynamic vacuum at 50 °C on the silica disk, which turned yellow-orange. After 1 h of reaction at 25 °C, the excess of **1a** was removed by reverse sublimation in a liquid nitrogen cooled tube, which was then sealed off using a torch. For each step, IR spectra were recorded. IR (**2a**): 2955, 2927, 2898, 2864, 2744, 1476, 1459, 1390, 1362 cm^{-1}. Anhydrous H_2 (70 000 Pa, 6.6 mmol) and 80 mg of **1a** (4.75% Re, 20.4 μmol Re) were heated at 250 °C for 86 h in a Schlenk tube (234 mL) to give 0.288 mmol of methane as the sole gaseous product according to GC analysis. This corresponds to a ratio of CH_4 evolved per Re of 14.1 or, in other words, 2.83 neopentyl-like ligand per Re. The reaction can be monitored by in situ IR spectroscopy using **2a** prepared in an IR-cell.

Reaction of 1a with Ph_3SiOH. In an NMR tube equipped with a Teflon screw cap (provided by Young Scientific Ltd.), Ph_3SiOH (12.0 mg, 43.5 μmol) was added at room temperature to a yellow-orange solution of **1a** (20.0 mg, 42.8 μmol) in 0.5 mL of C_6D_6. Ph_3SiOH slowly dissolved, and the color turned brown-red. Monitoring the reaction by ^{1}H NMR spectroscopy showed the complete disappearance of **1a** after 12 h at room temperature with the concomitant formation of neopentane and **2m** as a 10 to 1 mixture of its syn and anti isomers. After evaporation of the reaction mixture, a red oil was obtained as an inseparable mixture of **2m** of its syn and anti rotamers in a 10/1 ratio. ^{1}H NMR (C_6D_6): major isomer (syn) δ 1.10 (s, 9H, $ReCH_2C(CH_3)_3$), 1.12 (s, 9H, $Re{\equiv}CC(CH_3)_3$), 1.24 (s, 9H, $Re{=}CHC(CH_3)_3$), 2.62 (d, $^2J_{HaHb}$ = 13.1 Hz, 1H, $ReCH_aH_b{}^tBu$), 3.07 (d, $^2J_{HaHb}$ = 13.1 Hz, 1H, $ReCH_aH_b{}^tBu$), 7.0−7.5 (m, 9H, Ph), 7.6−8.0 (m, 6H, Ph), 10.86 (s, 1H, $Re{=}CH{}^tBu$) ppm. ^{13}C NMR: δ 29.5 ($Re{\equiv}CC(CH_3)_3$), 31.6 ($Re{=}CHC(CH_3)_3$), 32.6 ($ReCH_2C(CH_3)_3$), 32.7 ($ReCH_2C(CH_3)_3$), 45.1 ($Re{=}CHC(CH_3)_3$), 48.0 ($ReCH_2{}^tBu$), 53.3 ($Re{\equiv}CC(CH_3)_3$), 128.0 (Ph), 130.0 (Ph), 135.5 (Ph), 137.4 (Ph), 245.9 ($Re{=}CH{}^tBu$, $^1J_{CH}$ = 116 Hz), 292.4 ppm ($Re{\equiv}C{}^tBu$). The following signals were discernible for the anti rotamer of **2m**. ^{1}H NMR (C_6D_6): δ 1.14 (s, 9H, $Re{\equiv}CC(CH_3)_3$), 1.16 (s, 9H, $ReCH_2C(CH_3)_3$), 1.21 (s, 9H, $Re{=}CHC(CH_3)_3$), 2.26 (d, $^2J_{HaHb}$ = 12.7 Hz, 1H, $ReCH_cH_d{}^tBu$), 3.22 (d, $^2J_{HaHb}$ = 12.7 Hz, 1H, $ReCH_cH_d{}^tBu$), 12.65 (s, 1H, $Re{=}CH{}^tBu$). ^{13}C NMR: δ 28.4 ($Re{\equiv}CC(CH_3)_3$), 29.4 ($Re{=}CHC(CH_3)_3$), 33.9 ($ReCH_2C(CH_3)_3$), 42.1 ($Re{=}CHC(CH_3)_3$), 46.8 ($ReCH_2{}^tBu$), 53.9 ($Re{\equiv}CC(CH_3)_3$), 253.8 ($Re{=}CH{}^tBu$, $^1J_{CH}$ = 159 Hz), 301.2 ($Re{\equiv}C{}^tBu$). The H and C assignments were established by DEPT 135, HSQC, and HMBC 2D NMR experiments. The syn assignment for the major rotamer is based on the difference in ^{1}H chemical shift and $^1J_{CH}$ coupling for the carbenic protons between the syn and anti rotamers.[1b]

Reaction of 1a with the Polyoligomeric Silsesquioxane 3. In an NMR tube equipped with a Teflon screw cap (provided by Young Scientific Ltd.), the polyoligomeric silsesquioxane **3** (12.0 mg, 43.5 μmol) was added at room temperature to a yellow-orange solution of **1a** (20.0 mg, 42.8 μmol) in 0.5 mL of C_6D_6. Compound **5** immediately dissolved, and the color turned brown-red. Monitoring the reaction by ^{1}H NMR spectroscopy showed the almost complete (>95%) disappearance of **1a** after 12 h at room temperature with the concomitant formation of neopentane and **2n** as a 10 to 1 mixture of its syn and anti isomers. After evaporation of the reaction mixture, an orange-red oil was obtained as an inseparable mixture of **2n** of its syn and anti rotamers in a 10/1 ratio. ^{1}H NMR (C_6D_6): major isomer (syn) δ 1.09 (s, 9H, $ReCH_2C(CH_3)_3$), 1.09−1.25 (br m, *c*-$CH(CH_2)_4$), 1.25 (s, $Re{=}CHC(CH_3)_3$), 1.37 (s, 9H, $Re{\equiv}CC(CH_3)_3$), 1.4−2.1 (br m, *c*-$CH(CH_2)_4$), 2.56 (d, $^2J_{HaHb}$ = 12.8 Hz, 1H, $ReCH_aH_b{}^tBu$), 3.00 (d, $^2J_{HaHb}$ = 12.8 Hz, 1H, $ReCH_aH_b{}^tBu$), 11.00 (s, 1H, $Re{=}CH{}^tBu$) ppm. ^{13}C NMR: δ 22.7, 22.9, 27.3, 27.5, 27.8, 28.0 (*c*-$CH(CH_2)_4$)), 29.7 ($Re{\equiv}CC(CH_3)_3$), 31.6 ($Re{=}CHC(CH_3)_3$), 32.5 ($ReCH_2C(CH_3)_3$), 32.6 ($ReCH_2C(CH_3)_3$), 45.1 ($Re{=}CHC(CH_3)_3$), 49.3 ($ReCH_2{}^tBu$), 53.4 ($Re{\equiv}CC(CH_3)_3$), 247.2 ($Re{=}CH{}^tBu$, $^1J_{CH}$ = 118.0 Hz), 291.4 ppm ($Re{\equiv}C{}^tBu$). The following signals were discernible for the anti rotamer, ^{1}H NMR (C_6D_6): δ 1.16 (s, 9H, $ReCH_2C(CH_3)_3$), 1.27 (s, 9H, $Re{=}CHC(CH_3)_3$), 1.39 (s, 9H, $Re{\equiv}CC(CH_3)_3$), 2.20 (d, $^2J_{HaHb}$ = 12.6 Hz, 1H, $ReCH_cH_d{}^tBu$), 3.14 (d, $^2J_{HaHb}$ = 12.6 Hz, 1H, $ReCH_cH_d{}^tBu$), 12.63 (s, 1H, $Re{=}CH{}^tBu$). ^{13}C NMR: δ 28.4 ($Re{\equiv}CC(CH_3)_3$), 29.3 ($Re{=}CHC(CH_3)_3$), 33.8 ($ReCH_2C(CH_3)_3$), 42.1 ($Re{=}CHC(CH_3)_3$), 47.3 ($ReCH_2{}^tBu$), 54.1 ($Re{\equiv}CC(CH_3)_3$), 254.9 ($Re{=}CH{}^tBu$, $^1J_{CH}$ = 156.8 Hz), 300.7 ($Re{\equiv}C{}^tBu$). The H and C assignments were established by HSQC and HMBC 2D NMR experiments. ^{29}Si NMR (C_6D_6): −99.9 (1Si), −65.7 (4Si), −65.2 (3Si).

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Supporting Information Available: NMR spectra and evolution of the ^{13}C label on the carbenic carbon in **1c** as a function of time (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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