CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200500401

Grafting of $[Mn(CH_2tBu)_2(tmeda)]$ on Silica and Comparison with Its Reaction with a Silsesquioxane

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Abstract: The reaction of $[Mn(CH_2tBu)_2(tmeda)]$ (**1**) and a silica partially dehydroxylated at 700°C ($SiO_{2/700}$) yields a single surface species $[(\equiv SiO)Mn(CH_2tBu)(tmeda)]$ (**2a**; tmeda = tetramethylethylendiamine), while a mixture of **2a** and $[(\equiv SiO)_2Mn(tmeda)]$ (**2b**) is obtained by using $SiO_{2/200}$, $SiO_{2/300}$, or $SiO_{2/500}$ as evidenced by mass balance analysis, and IR and EPR spectroscopy. The reaction of **1** and $(c\text{-}C_5H_9)_7Si_7O_{12}SiOH$ (**3**), a soluble silanol that is a molecular model for a silica support, generates the bis-siloxy complex **4**, $[\{(c\text{-}C_5H_9)_7Si_7O_{12}SiO\}_2Mn(tmeda)_2]$, in a quantitative yield; compound **4** was characterized by single-crystal X-ray diffraction. These reactions exemplify the limitation of considering molecular silanol derivatives as straightforward and reliable homogeneous models for silica, and address the need for thorough characterization of surface species by the use of surface-science techniques. These studies show the possibility of preparing coordinatively and geometrically unique surface species that would be difficult to prepare by solution chemistry methods; insights into the chemical and physical properties of these surface species are also gained.

Keywords: manganese · silica · silsesquioxane · surface chemistry

Introduction

Surface organometallic chemistry is a technique that is useful for preparing well-defined surface complexes. The molecular environment of the grafted species is elucidated by spectroscopic studies, from which structure–reactivity relationships may be developed.[1]

The understanding of how organometallic compounds are attached to a solid support, such as silica, is an essential feature of surface organometallic chemistry. This information is obtained by traditional methods of analysis, such as the amount of volatile gases evolved during grafting, elemental composition of the resulting material, and reactivity studies on the modified surface. Physical techniques, such as EXAFS, and solid-state NMR and IR spectroscopy are useful for addressing the coordination geometry and structure of the grafted compounds. An additional strategy has been to compare the physical and chemical properties (vibrational frequencies,[2–4] NMR chemical shifts[5,6] and elementary steps involved in the grafting reaction of the organometallic precursor on a surface)[5] of the grafted compounds with those of simpler model compounds[7–12] that are obtained by homogeneous methodologies.

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In this paper, we show that ESR spectroscopy of the species formed by grafting [Mn(CH_2*t*Bu$)_2$(tmeda)] (**1**; tmeda = tetramethylethylendiamine)[13,14] on SiO_2 (dehydroxylated at various temperatures) is a useful structural probe for the paramagnetic Mn^{II} species. The potential molecular analogue [{(*c*-$C_5H_9)_7Si_7O_{12}SiO\}_2$Mn(tmeda$)_2$] isolated from the reaction of **1** and a silsesquioxane, (*c*-$C_5H_9)_7Si_7O_{12}SiOH$ (**3**), has been characterized by X-ray diffraction.

Results and Discussion

Reaction of [Mn(CH_2*t*Bu$)_2$(tmeda)] (1) with silica partially dehydroxylated at various temperatures: The reaction of [Mn(CH_2*t*Bu$)_2$(tmeda)] (**1**) has been carried out on silica partially dehydroxylated at 200, 300, 500, and 700 °C (i.e. $SiO_{2/200}$, $SiO_{2/300}$, $SiO_{2/500}$, and $SiO_{2/700}$, respectively). The temperature of dehydroxylation of the support is related to the different concentrations of surface silanols (Table 1), and this is a key parameter in determining the structure of the grafted complex.[15–17]

Table 1. Stoichiometric ratios of reagents (Mn in solution, and ≡SiOH on $SiO_{2/T}$) metal elemental analyses of solids $\mathbf{2}_T$ thus obtained, and neopentane amount evolved during the grafting syntheses. The syntheses were performed by impregnation of **1** in pentane, at room temperature, onto silica partially dehydroxylated at various temperatures ($T = 200$, 300, 500, and 700 °C).

T [°C] [a]	Mn_0/≡SiOH[b]	$Mn_{grafted}$ [% wt][c]	*t*BuCH_3[d] obsd (theory)[e]	$[Mn]_{grafted}/[Mn]_0$ [%]	$[≡SiO-]_{reacted}/[≡SiOH]_0$ [%][e]
200	1.18	3.04	1.5 (1.6)	54	100
300	1.14	2.75	1.4 (1.4)	67	100
500	1.0	2.1	–	96	103
	1.6	2.23	1.1 (1.1)	67	105
700	1.03	1.17	1.0 (1.0)	76	79
	1.28	1.14	1.0 (1.0)	60	77
	1.22	1.3	1.2 (1.0)	72	88
	1.39	1.51	1.0 (1.0)	73	100

[a] Dehydroxylation temperature. [b] Reactant stoichiometic ratio based on [**1**] for Mn_0 and surface concentration of ≡SiOH for $SiO_{2/T}$ (i.e., 0.86, 0.70, 0.4, and 0.27 mmol g^{-1} ($SiO_{2/T}$) for $T = 200$, 300, 500, and 700 °C, respectively). [c] Percentage of manganese determined by elemental analysis of solids $\mathbf{2}_T$ [d] 2,2-Dimethylpropane (*t*BuCH_3) evolved during impregnation and quantified by GC (mmol *t*BuCH_3mmol^{-1} Mn grafted on $\mathbf{2}_T$). [e] The expected values are calculated under the hypothesis that $\mathbf{2}_T$ are decorated by surface species **2a** and **2b** in a relative ratio of 4:6, 6:4, 9:1, and 1:0 for $T = 200$, 300, 500, 700 °C, respectively (see text for further explanations).

Characterization by IR spectroscopy: Typically, a silica pellet (20 mg) was treated at the desired temperature (200–700 °C) for 12 h under dynamic vacuum (10^{-5}Torr) and then immersed in a colorless solution of complex **1** in pentane. After 4 h, the pellet was washed twice with pentane for 30 min and dried under vacuum. For the experiment performed on $SiO_{2/700}$, the IR peaks associated with the isolated surface silanols (3745 cm^{-1}) completely disappeared (Figure 1). Conversely, new IR bands associated with the ν(C−H) and δ(C−H) of alkyl ligands are observed in the 3000–2760 cm^{-1} and 1470–1350 cm^{-1} regions, respectively. Grafting on silica pre-treated at lower dehydroxylation temperatures provides the same qualitative observations except that the intensity of the wide band characteristic of associated surface silanols (3700–3400 cm^{-1}), which are not accessible to bulky reactants such as alkylating agents, does not change.[18,19]

These observations, in particular the disappearance of the surface silanol stretching bands, as well as the formation of 2,2-dimethylpropane in the gas phase (vide infra) are consistent with the chemical grafting of the complex **1** onto the silica surface.

Mass balance analysis: To obtain accurate data on gas evolution during grafting, the reaction was carried out on larger scales (typically, 0.5–1.0 g of silica) by stirring a suspension of silica partially dehydroxylated at the desired temperature, $SiO_{2/T}$ (*T* in °C), in a solution of [Mn(CH_2*t*Bu$)_2$(tmeda)] in pentane with metal concentrations ranging from 1.0 to 1.4 equivalents per surface ≡SiOH groups (see Table 1). After filtration and washing cycles, all volatile compounds were condensed into another reactor of known volume in order to quantify 2,2-dimethylpropane evolved during grafting. The resulting white solids $\mathbf{2}_T$ were further dried under dynamic vacuum (10^{-5} Torr) and characterized by elemental analysis (Tables 1 and 2).

Gas evolution during grafting and elemental analyses of the resulting solids $\mathbf{2}_T$ greatly varies depending on the temperature of partial dehydroxylation of the support (*T*).

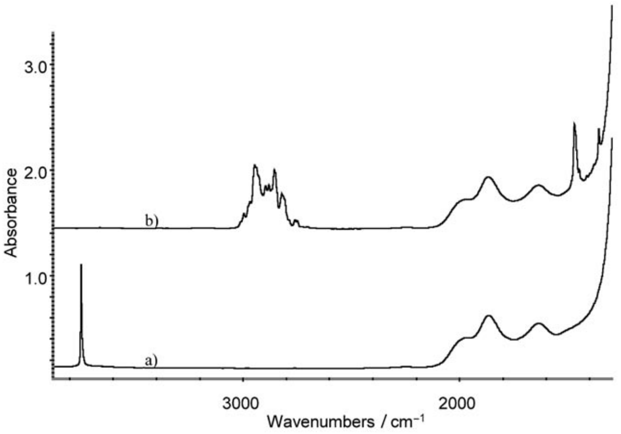


Figure 1. Monitoring of the grafting of complex **1** onto silica partially dehydroxylated at 700 °C using IR spectroscopy. a) silica pellet (25.2 mg) partially dehydroxylated 12 h at 500 °C and 4 h at 700 °C. b) After impregnation of a) in a solution of **1** in pentane for 4 h followed by two washing steps in pentane.

Table 2. Elemental analyses of the solid $\mathbf{2}_T$ resulting from the impregnation with **1** in pentane, at room temperature, onto $SiO_{2/T}$, silica partially dehydroxylated at various temperatures.

T [°C][a]	Mn [% wt]	C [% wt]	H [% wt]	N [% wt]	C/Mn obsd (theory)[b]	H/Mn obsd (theory)[b]	N/Mn obsd (theory)[b]	C_{tot}[c] obsd (theory)
200	2.31	3.54	–	1.18	7 (8)	–	2 (2)	16 (16)
	3.04	4.69	0.79	1.56	7 (8)	14 (17)	2 (2)	15 (16)
300	2.75	4.15	–	1.28	7 (9)	–	2 (2)	14 (16)
500	2.1	4.45	1.39	1.41	9 (10)	24 (25)	2 (2)	15 (16)
700	1.17	3.01	–	0.71	12 (11)	–	2 (2)	17 (16)
	1.14	2.76	0.62	0.87	11 (11)	30 (27)	3 (2)	17 (16)
	1.3	2.92	0.67	0.8	10 (11)	28 (27)	2 (2)	16 (16)
	1.51	3.63	0.77	0.82	11 (11)	28 (27)	2 (2)	16 (16)

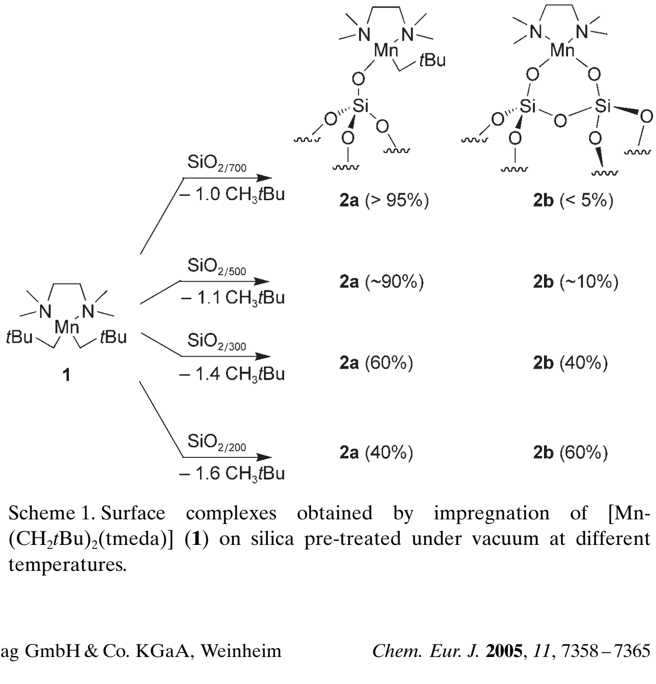
[a] Dehydroxylation temperature in °C. [b] Expected values are calculated under the hypothesis that $\mathbf{2}_T$ contain surface species **2a** and **2b** in a relative ratio of 4:6, 6:4, 9:1, and 1:0 for $T=200$, 300, 500, 700 °C, respectively (see text for further explanations). [c] The errors on the analyses are ±1 a.m.u. for C and N, and ±2 a.m.u. for H. [d] Mass balance of total carbon atoms (C_{tot}) based on $tBuCH_3$ evolved/Mn (see Table 1) and % wt C/Mn.

When silica is dehydroxylated at 700 °C, 1.05 equivalents of 2,2-dimethylpropane are evolved per grafted Mn for all the impregnations performed (see Table 1). When the reaction is performed on deuterated silica, 80 % of the neopentane formed is monodeuterated. These results indicate that the grafting reaction involves mainly the silanolysis of one metal–alkyl group by the surface ≡SiOH (or ≡SiOD) moieties.

The manganese loadings obtained on $\mathbf{2}_{700}$ (1.2–1.5 % wt) depend on the quantity of **1** present in the impregnation solution; the maximum Mn-loading (1.51 % wt, that is, 0.27 mmol Mn g^{-1} silica) is obtained when an excess of **1** is used (see Table 1) and corresponds to the amount of silanol available on $SiO_{2/700}$ (0.27 mmol OH per g silica). These data suggest that the grafting reaction involves one surface silanol per grafted metal atom. Finally, the C, H, and N elemental analyses on $\mathbf{2}_{700}$ show, on average, the presence of 11 ± 1 C, 29 ± 1 H, and 2 ± 1 N per surface Mn atom, which is in good agreement with that expected for a monosiloxy surface species [(≡SiO)Mn(CH_2tBu)(tmeda)] (**2a**), which should be 11, 27, and 2 for C, H, and N per Mn, respectively (Scheme 1). Therefore, species **2a** is the principal product formed on $SiO_{2/700}$ independent of the relative concentration between the molecular precursor and the surface ≡SiOH moieties available during impregnation (Table 1).

When silica is dehydroxylated at 500 °C, similar data as those collected for $SiO_{2/700}$ are obtained, that is 1.1 $tBuCH_3$/grafted Mn, elemental analysis close to the expected values for the presence of **2a** as the major surface species (vide infra for further comments on $\mathbf{2}_{500}$), and a maximum loading of 1 Mn/≡SiOH. Higher concentrations of grafted manganese are obtained on $SiO_{2/500}$ than on $SiO_{2/700}$; the maximum loading in the former is 2.23 % wt, that is, 0.40 mmol Mn g^{-1}. This is in agreement with the high amount of OH available on $SiO_{2/500}$. Conversely, at lower pre-treatment temperatures of the starting silica (300 °C and 200 °C), a different reactivity pattern is observed. Slightly higher metal loadings are achieved (2.3–3.0 % wt) despite the much higher concentration of surface ≡SiOH (0.86 mmol g^{-1} for $SiO_{2/200}$), and more 2,2-dimethylpropane per grafted Mn is observed, that is, 1.4 and 1.6 equivalents per grafted Mn for $SiO_{2/300}$ and $SiO_{2/200}$, respectively. This indicates that the chemical grafting of **1** on the respective silica surface occurs through the silanolysis of 1.4 and 1.6 metal–alkyl bonds per metal center by the surface ≡SiOH moieties. The elemental analyses of the resulting solids are consistent with the co-existence of two surface species: the monosiloxy species **2a** and the bis-siloxy species [(≡SiO)$_2$Mn(tmeda)] (**2b**) in a 6:4 and 4:6 ratio, for $SiO_{2/300}$ and $SiO_{2/200}$, respectively. The formation of the bis-siloxy species results from the reaction of one metal center with two vicinal ≡SiOH moieties. The observed larger proportion of **2b** on silica dehydroxylated at lower temperatures is consistent with the increased probability of finding two vicinal ≡SiOH moieties on silica with a higher silanol content, which in turn decreases the metal loading (Figure 2).

In conclusion, according to mass balance analysis and IR spectroscopy, the reaction of [Mn(CH_2tBu)$_2$(tmeda)] with silica ranging from $SiO_{2/200}$ to $SiO_{2/700}$ yields different solids, $\mathbf{2}_T$ ($T=200$, 300, 500, and 700 °C). While complex **2a** is obtained on $SiO_{2/500}$ and $SiO_{2/700}$, with different maximum loadings, an approximate 1:1 mixture of complexes **2a** and **2b** is



Scheme 1. Surface complexes obtained by impregnation of [Mn(CH_2tBu)$_2$(tmeda)] (**1**) on silica pre-treated under vacuum at different temperatures.

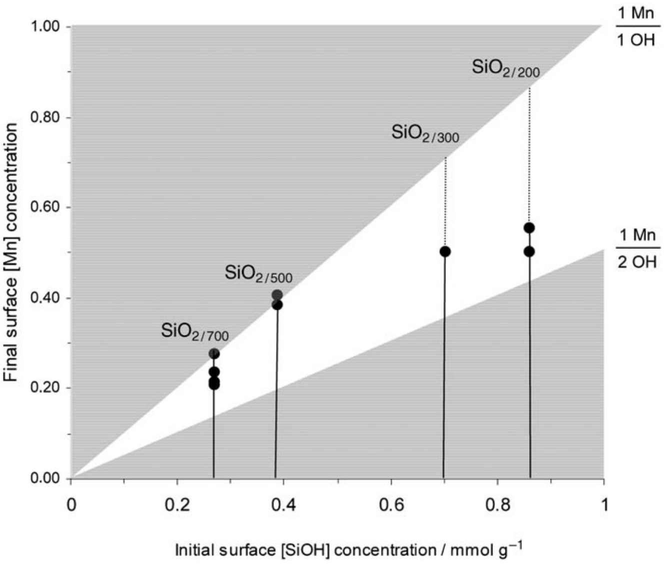


Figure 2. Plot of the observed final grafted Mn concentration of $\mathbf{2}_T$ versus the initial surface $\equiv$SiOH concentration of the starting silica, $SiO_{2/T}$ ($T=$ 200, 300, 500, and 700 °C). Concentration expressed in mmol g^{-1} silica. The predicted area of accessible concentrations for [Mn] in $\mathbf{2}_T$ (Mn: OH relative ratios between 1.0 and 0.5) based on surface organometallic considerations discussed in the text is shaded in white.

found on silica partially dehydroxylated at lower temperatures.

Characterization by ESR spectroscopy: ESR spectra of the molecular complex $[Mn(CH_2tBu)_2(tmeda)]$[13,14] and of the supported species $\mathbf{2}_T$ have been recorded. The ESR spectra of a frozen solution ($T=140$ °C) of the precursor complex **1** in toluene at X- and Q-band frequencies are shown in Figure 3.

At X-band (Figure 3 top), the most pronounced lines are found at 80, 87, 163, 211, 253, 519, 558, and 706 mT. For some low-field lines the manganese hyperfine interaction is resolved (nuclear spin of $^{55}Mn=5/2$) resulting in a sextet with hyperfine splitting, $A(^{55}Mn)=3.2$ mT.

ESR spectra of **1** with similar spectral features, which may be observed up to 1.1 T, have been analyzed using the D-B plot method in the literature.[13] Common features of the spectra are intense bands around 150 mT ($g_{\mathrm{eff}}\approx 4.3$ region). Such a feature commonly arises in a so-called “rhombic” symmetry for high-spin d^5 complexes, which are characterized by D values greater than about 0.23 cm^{-1} and λ values ($\lambda=E/D$) close to 1/3. Griffith has shown that a tetrahedral high-spin manganese(II) complex of the type MA_2B_2 should give this type of spectrum.[20,21] Analogous spectra have also been observed in (slightly distorted) tetrahedral manganese compounds. The spectra are assigned to Hamiltonian parameters $D=0.42$ cm^{-1}, $\lambda=0.23$.[20–26] The spin Hamiltonian of the system can be expressed by Equation (1).

$$H = g\beta BS + D[S_z^2 - \frac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) \qquad (1)$$

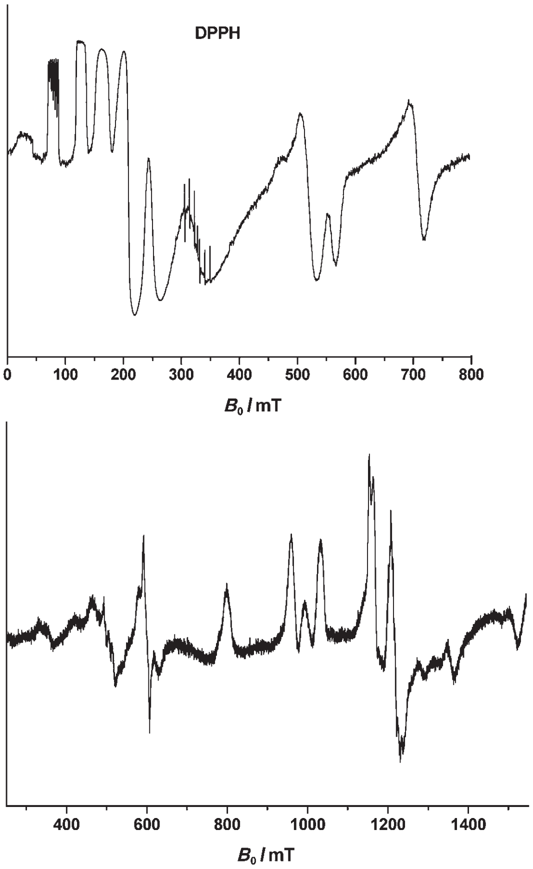


Figure 3. Top: X-band ESR spectrum of a frozen solution **1** in toluene, $T_{\mathrm{rec}}=130$ K, $\nu=9.05$ GHz, microwave power: 5 mW. Bottom: Q-band ESR spectrum of a frozen solution **1** in toluene, $T_{\mathrm{rec}}=130$ K, $\nu=$ 34.57 GHz, microwave power: 1 mW.

Spectra simulations for the system under study yield the same D and λ values ($D=0.42$ cm^{-1}, $\lambda=0.23$).[27] The Q-band measurements of the precursor complex (Figure 3 bottom) confirm the values for D and λ given above and show that all lines observed belong to the precursor complex.

The ESR spectra of complex **1** grafted onto the silica surfaces (solids $\mathbf{2}_T$) show similar features as discussed above, with clearly increased line widths, as expected. The ESR spectrum of solid $\mathbf{2}_{300}$ shows a sigmoidal shape with two maxima at 206.6 and 290 mT and a minimum at 370 mT, while the ESR spectrum of $\mathbf{2}_{700}$ displays a different sigmoidal curve with two maxima at 103.3 and 206.6 mT and a minimum at 250 mT (Figure 4). The spectrum of $\mathbf{2}_{500}$ corresponds to a superposition of the two previous spectra in accordance with elemental analysis. These observations are consistent with the geometrical changes of surface Mn species, which arise from differences in the temperature of thermal pretreatment of the support. In accordance with the elemental analysis, the two different ESR spectra can be assigned to species **2a** and **2b**. Accordingly, the spectrum of $\mathbf{2}_{700}$ (Figure 4) is due to a unique surface species **2a**, whose structure resembles that of **1**, in which one neopentyl ligand has been replaced by a surface siloxy group.

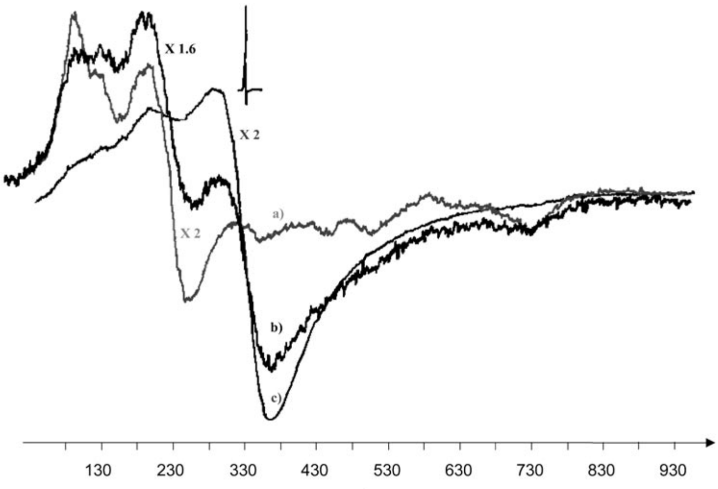


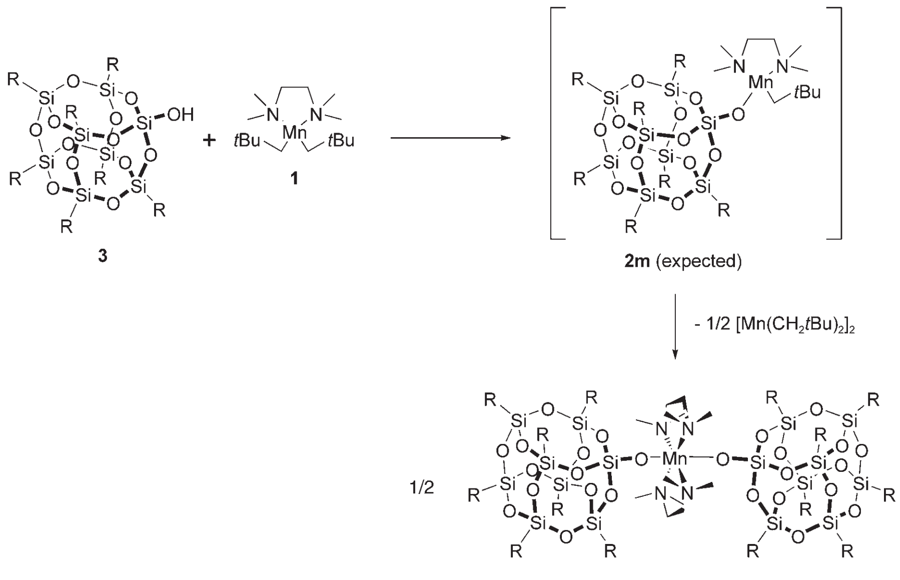
Figure 4. ESR spectra recorded at room temperature, of **1** grafted on silica partially dehydroxylated at different temperatures: a) **1**/$SiO_{2/700}$; b) **1**/$SiO_{2/500}$; c) **1**/$SiO_{2/300}$.

All the ESR spectra of the unsupported and supported complexes are due to well defined, isolated, high-spin Mn^{II} complexes that have a distorted tetrahedral geometry. Changes and shifts in the spectral features are consistently explained by changing an alkyl ligand by an alkoxide ligand on the Mn site, and by changes in symmetry around the manganese center. The lower symmetry of the surface complexes in comparison to the precursor is also reflected by varied relaxation times; the spectra of the grafted complexes are easily observable even at room temperature.

Reactivity of the supported species ***2a***: The surface complex **2a** reacts slowly and not quantitatively with H_2O to release 2,2-dimethylpropane (0.7 equiv in 24 h). Similarly, its reaction with H_2 at 150 °C gives only small amount of 2,2-dimethylpropane (0.1 equiv), and no hydride is formed according to IR spectroscopy. These data are in sharp contrast to what is observed for silica-supported Group 4 and 5 transition metals.[1] Additionally, **2a** does not react with CO or ethylene. However, it violently reacts with O_2 to give a brown-black material, probably resulting from an over oxidation reaction, while it is unreactive towards N_2O. Finally, a clean single-electron oxidation is observed as **2a** quantitatively reacts (titration) with one equivalent of ferrocinium hexafluorophosphate $[(Cp)_2Fe]^+PF_6^-$ (blue), giving an orange solution (ferrocene) and a white-grey solid (not characterized), as expected from the thermodynamic data [Eq. (2), $(Cp)_2Fe^+/CpFe$ couple = 0.4 eV, Mn^{II}/Mn^{III} couple = 1.54 eV).

$$[(Cp)_2Fe]^+PF_6^- + [Mn^{II}L_n] \rightarrow [(Cp)_2Fe] + [Mn^{III}L_n]^+PF_6^- \qquad (2)$$
$$\Delta G^o = -25.9\,\text{kcal mol}^{-1}$$

Molecular modeling by using a silsesquioxane: The reaction of complex **1** with the silsesquioxane $(c\text{-}C_5H_9)_7Si_7O_{12}SiOH$ (**3**) has been performed with the goal of obtaining molecular compounds that model the proposed structures **2a** and **2b**. The only isolable product obtained is the bis-siloxy Mn^{II} complex $[\{(c\text{-}C_5H_9)_7Si_7O_{12}SiO\}_2Mn(tmeda)_2]$ (**4**), even when the molar ratio of **3**/**1** is 2:1 (Scheme 2). No monosiloxy derivative was obtained by reaction of the silsesquioxane with the Mn^{II}–dialkyl precursor **1**, even when 0.9 equivalents of the silanol was slowly added to a solution of **1** in toluene. Pale yellow single crystals of **4** were obtained in a quantitative yield (based on the limiting reagent) by a slow diffusion of acetonitrile into the saturated benzene solution of the reaction mixture. The structure of **4** determined by X-ray diffraction studies on single crystals indicates a Mn^{II} center in an octahedral geometry, with the two silsesquioxane ligands in a *trans* arrangement and two bidentate tmeda ligands in the equatorial plane (Figure 5). The Mn–O and average Mn–N distances for **4** are 2.040(2) and 2.41(2) Å, respectively, and they are comparable with those obtained for the only other mononuclear siloxy Mn compound, $[Mn\{OSi(OtBu)_3\}_2(py)_3]$ (**5**; 1.980 and 2.33 Å, respectively), which displays a Mn^{II} center in a trigonal-bipyramidal geometry.[28] Noteworthy,



Scheme 2. Reactivity of **1** with **3**.

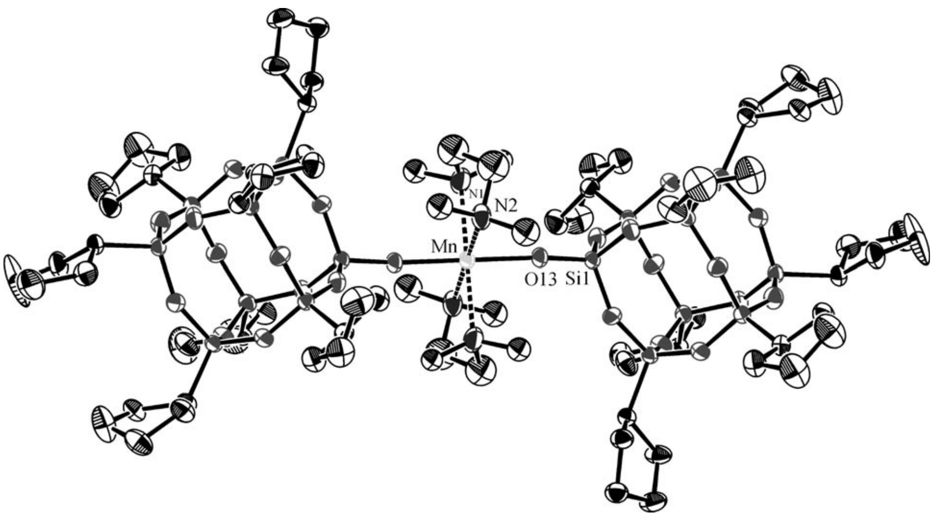


Figure 5. ORTEP representation[34] of compound **4** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Only one position of the disordered tmeda molecules is shown. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Mn–N1 2.370(5), Mn–N2 2.452(3), Mn–O13 2.040(2), Si1–O13 1.556(2); N1-Mn-N2 82.2(1), O13-Mn-N1 88.9(1), O13-Mn-N2 88.0(1), O13-Mn-O13[a] 180, Mn-O13-Si1 168.3(2). Symmetry code: $-x$, $-y$, $-z$.

both complexes **4** and **5** share 1) the oxidation state of the metal, Mn^{II}, 2) the presence of only siloxy groups as anionic ligands, 3) the *trans* configuration of the siloxy ligands, and 4) the presence of amine ligands to complete the coordination sphere of the Mn^{II} center. This *trans* configuration of the two siloxy groups is probably unlikely to be present in a surface species. This structure shows the limitation of using silsesquioxane as a homogenous model for a surface species, particularly when the solution complexes have low coordination numbers and/or when ligand exchange is rapid. Similarly, the reaction of $[O(Ph_2SiOH)_2]$ with $[Mn\{N(SiMe_3)_2\}_2]$ generates the trisnuclear phenyldisiloxy complex Mn^{II} $[\{(Me_3Si)_2N\}_2Mn_3\{O(Ph_2SiO)_2\}_2]\cdot 2\,THF$.[29] Such differences show that surface species can achieve different configurations (e.g., a *cis* arrangement, when the thermodynamic product would favor a *trans* arrangement, as in solution) and lower coordination numbers (4 vs 6) at a metal center with respect to their solution analogue.

Conclusion

From mass balance measurements, and IR and ESR spectroscopy, it was possible to show that the complex $[Mn(CH_2tBu)_2(tmeda)]$ (**1**) reacts with silanols of a silica surface to form either $[(\equiv SiO)Mn(CH_2tBu)(tmeda)]$ (**2a**) on $SiO_{2/700}$, or a mixture of **2a** and $[(\equiv SiO)_2Mn(tmeda)]$ (**2b**) on silica partially dehydroxylated at lower temperatures, for example, for $SiO_{2/200}$. Attempts to model impregnation syntheses by solution chemistry by studying the reaction of **1** with $(c\text{-}C_5H_9)_7Si_7O_{12}SiOH$ (**3**) give the bis-siloxy complex $[\{(c\text{-}C_5H_9)_7Si_7O_{12}SiO\}_2Mn(tmeda)_2]$ (**4**) in a quantitative yield with respect to the limiting reactant.

The different reactions show the limitation of using molecular silanol derivatives as homogeneous soluble models for surface species, particularly when the solution complexes have low coordination numbers or when ligand exchange reactions are rapid. Thus, thorough characterization of surface species by the use of several chemical and physical techniques is essential. The differences between the surface species **2a** and **2b** and the molecular complex **4** exemplify the advantage that surface chemistry offers relative to solution chemistry, namely, surface organometallic chemistry provides access to coordinatively and geometrically unique surface species that would be difficult to obtain in solution; it also illustrates the concept of site isolation in heterogeneous catalysis. These points play a critical role in explaining the unique catalytic properties of some heterogeneous catalysts.

Experimental Section

Generals conditions and starting material: All experiments were carried out in the strict absence of oxygen and water. Glove box or standard Schlenck techniques under Ar were used for organometallic syntheses. Pentane and toluene were distilled over Na/K amalgam, degassed by four freeze-pump-thaw cycles and stored under Ar over 3 Å molecular sieves. Diethyl ether, benzene, dioxane, and THF were distilled over Na/benzophenone mixture. 2,2-Dimethylpropylmagnesium chloride was prepared from 2,2-dimethylchloropropane (Aldrich, 99%) and Mg turnings (Lancaster). Tetramethylethylenediamine (Aldrich) was distilled over Na and stored over 3 Å molecular sieves. $MnCl_2$ (Strem Chemicals, 98%) was heated at reflux with $SOCl_2$ and dried at 150°C under vacuum before use. H_2 was dried over a deoxo catalyst (BASF R3–11 + 3 Å molecular sieves) prior to use. Carbon monoxide, ethylene, and oxygen were dried over 3 Å molecular sieves prior to use. $[(c\text{-}C_5H_9)_7Si_7O_{12}SiOH]$ (Aldrich) was heated at 40°C for 12 h at 10^{-5} Torr before use. Silica (Degussa Aerosil®, 200 m^2g^{-1}) was calcined at 200°C in air for 2 h, treated at 200°C under high vacuum (10^{-5} mmHg) for 12 h (support referred to as $SiO_{2/200}$). The preparation of the surface $SiO_{2/300}$ and $SiO_{2/500}$ was achieved by similar procedures with temperatures of calcination and treatment under vacuum of 300 and 500°C, respectively. For $SiO_{2/700}$, $SiO_{2/500}$ was treated at 700°C for 4 h.

IR spectra were recorded on a Nicolet Magna 550-FT spectrometer equipped with a cell designed for in situ preparation under controlled atmosphere. Gas-phase analyses were performed on a gas chromatograph HP 5890 equipped with a flame ionization detector and a Al_2O_3/KCl on fused column (50 m × 0.32 mm). Elemental analyses were performed by the CNRS Central Analysis Service of Solaize and by the Mikroanalytisches Labor Pascher Remagen in Germany. Mass spectroscopy by electronic impact was recorded on a FINNIGAN MAT95XL spectrometer.

ESR spectroscopy: The ESR spectra of **1** were recorded on a Jeol JES RE2X at X-band frequency at temperatures between 130 and 298 K; microwave frequency about 9.05 GHz, microwave power 2–5 mW, modulation frequency 100 kHz, modulation amplitude 0.4 mT. The *g* values were determined with a NMR magnetometer and Mn^{2+} in MgO as *g* marker. The ESR parameters were obtained by comparison of experimental and simulated spectra (simulation program: Matlab^{TM} EasySpin EPR simulation toolbox[27]). Q-band ESR spectra (Bruker EMX) were recorded at temperatures of 130 K; microwave frequency about 34 GHz, modulation frequency 70 kHz, modulation amplitude 0.8 mT. The ESR spectra of $\mathbf{2}_T$ were performed on an ESR Spectrometer VARIAN E9.

Preparation of [Mn(CH$_2$*t*Bu)$_2$(tmeda)] (1): Complex **1** was synthesized according to literature procedure (see details in the Supporting Information).[13,14]

Preparation of $\mathbf{2}_T$ by the reaction of complex 1 with silica by impregnation: A representative procedure is as follows: Large-scale impregnations were typically carried out by adding at room temperature a solution of **1** (60 mg) in of pentane (10 mL) to silica partially dehydroxylated at the desired temperature SiO$_{2/T}$ (0.50 g), to achieve the relative ratios reported in Table 1. After 4 h, the solid was filtered and washed five times with pentane. The solution was evaporated, and the gas phase trapped in a 5 L flask cooled with liquid N$_2$; the gases thus trapped were analyzed by GC (see Table 2). The remaining solid was then further dried under vacuum (10^{-5} mmHg) to yield the white powders $\mathbf{2}_T$. A similar procedure was used for the in situ IR studies, for which a self-supporting silica disk was used in place of silica powder. Typically, the silica pellet (ca. 20 mg) prepared as described in general procedures was dipped in a solution of **1** in pentane (10 mL) for 4 h at room temperature, washed twice with pentane (10 mL) and then dried under vacuum; the IR spectra were then recorded.

Reactivity of 1 with [(*c*-C$_5$H$_9$)$_7$Si$_7$O$_{12}$SiOH] (3): Compound **3** (160 mg, 0.17 mmol) was added to a solution of **1** (54.7 mg, 0.17 mmol) in benzene (2 mL). This solution was stirred for 8 h and filtered with a cannula through a Teflon pad. In a 10 mm tube, pure benzene (2 mL) followed by of acetonitrile (4 mL) were successively added to the reaction mixture. After one week at room temperature, several slight yellow crystals appeared (54 % yield based on **3**). Elemental analysis calcd (%) for **4** (C$_{82}$H$_{158}$N$_4$Mn$_1$Si$_{16}$O$_{26}$): C 46.44, H 7.51, N 2.64, Mn 2.59, Si 21.19; found: C 44.88, H 7.67, N 2.69, Mn 3.12, Si 19.67.

Suitable single crystals for the X-ray diffraction study were grown by slow diffusion of acetonitrile into a saturated solution of **4** in benzene at room temperature. C$_{82}$H$_{158}$MnN$_4$O$_{26}$Si$_{16}$, $M_r=2120.51$, colorless to pale yellow fragment ($0.12\times0.25\times0.36$ mm^3), monoclinic, $P2_1/c$ (No.: 14), $a=12.0488(1)$ $b=23.3311(3)$, $c=19.4709(3)$ Å, $\beta=96.9005(5)°$, $V=5433.85(12)$ Å^3, $Z=2$, $\rho_{\text{calcd}}=1.296$ g cm^{-3}, $F_{000}=2270$, $\mu=0.366$ mm^{-1}. Preliminary examination and data collection were carried out on an area detecting system (NONIUS, MACH3 κ-CCD) at the window of a rotating anode (NONIUS, FR591) and graphite monochromated Mo$_{K\alpha}$ radiation ($\lambda=0.71073$ Å). The unit cell parameters were obtained by full-matrix least-squares refinement of 9962 reflections.[30] Data collection were performed at 123 K within a θ range of $1.37<\theta<25.23°$. Seven data sets were measured in rotation scan modus with $\Delta\phi/\Delta\omega=1.0°$. A total of 83 073 intensities were integrated. Raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure, for latent decay and absorption effects.[31] After merging ($R_{\text{int}}=0.043$), 9766 [8125: $I_o>2\sigma(I_o)$] independent reflections remained and all were used to refine 585 parameters. All non-hydrogen atoms of the ordered part of the molecule and the two nitrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were calculated in ideal positions (riding model). The refinements converged with $R1=0.0528$ [$I_o>2\sigma(I_o)$], $wR2=0.1535$ (all data), and GOF = 1.062. The final difference Fourier map showed no striking feature ($\Delta e_{\text{min/max}=}+1.08/-0.70$ e Å^{-3}). The tmeda ligand appears to be disordered over two positions (50:50). For this reason the carbon atoms had to be refined with isotropic displacement parameters. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography.[32] All calculations were performed with the STRUX-V[33] system including the programs PLATON,[34] SIR92,[35] and SHELXL-97.[36]

CCDC-258959 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We are grateful to the CNRS, CPE Lyon and the Centre de Coopération Franco-Bavarois for financial supports. V.R. and R.R.A. thank the Région Rhône-Alpes and the CNRS for pre-doctoral and visiting scientist fellowships, respectively.

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Received: April 8, 2005