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Reactivity of Anhydrous Keggin-Type Heteropolyacids with Alkylsilanes: Synthesis and Characterization

Eva Grinenval, Jean-Marie Basset, and Frédéric Lefebvre*

Université de Lyon, Institut de Chimie de Lyon, Lyon, France; Université Lyon 1; CPE Lyon; CNRS, UMR C2P2, LCOMS; Bâtiment CPE Curien; 43 Boulevard du 11 Novembre 1918; F-69616, Villeurbanne, France

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Anhydrous tungstic heteropolyacids react with alkylsilanes in the absence of solvent, leading to the evolution of hydrogen and the formation of a new kind of species where silicon is only weakly interacting with the polyoxometalate. The resulting material was characterized by various physicochemical methods including NMR, IR, and Raman spectroscopy. The most interesting feature is the unusual chemical shift of the ^{29}Si nuclei (ca. +50 ppm), which confirms the formation of a quasi-ionic bond between the organic and inorganic moieties. The weakness of this bond was also evidenced by chemical reactivity with nBu$_4$NCl (leading to the formation of R$_3$SiCl species) and oxygen. This new kind of structure can be of great interest in the field of microelectronics. Indeed the reactivity described in this article can be used and transferred easily in heterogeneous conditions to introduce defects in semiconductors.

Introduction

Polyoxometalates are constituted by early transition metals in their highest oxidation states and oxo anions. This class of inorganic compounds is of increasing interest owing to its wide range of properties and applications in areas from catalysis to medicine including materials science.[1,2] The polyoxometalates reveal indeed an important molecular and electronic structural diversity from small to nanosized species. Their structures are based upon $\{MO_p\}$ and $\{XO_q\}$ polyhedra sharing usually vertices or edges (Figure 1).

Polyoxometalates have especially received much attention in the area of catalysis because their chemical properties such as redox potentials, acidities, and solubilities can be tuned by choosing the constituent elements.[3−6] Among the derivatization of the polyoxometalates including organometallic components, three kinds of species can be found: (i) polyoxometalate-incorporated organometallic complexes; (ii) organometallic complexes capped on a polyoxometalate, and (iii) organometallic cation salts of polyoxometalate anions.

In polyoxometalate-incorporated organometallic complexes, the organometallic moiety is incorporated into a vacancy of the polyoxometalate framework. The first reported organometallic polyoxometalate, $[PW_{11}O_{39}(TiCp)]^{4-}$, was obtained by reaction of $(n\text{-Bu}_4N)_4[H_3PW_{11}O_{39}]$ with CpTiCl$_3$.[7] A very wide range of compounds with many vacancies (including mono- to tri-vacant polyoxometalates), structures (including monomeric to tetrameric structures), and various metals (including both noble and transition metals) have then been developed.[8−16] Transition-metal-substituted polyoxometalates are oxidatively and hydrolytically stable compared to organometallic complexes. Thus, the main interest of these compounds is the control of the active site which has been applied to the development of bio-mimetic catalysts.[3]

Organometallic complexes capped on polyoxometalate are made of non lacunar polyoxometalates which are able to covalently bond organometallic complexes owing to the charge density at their surface oxygens. Note that the surface

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*To whom correspondence should be addressed. E-mail: lefebvre@cpe.fr.

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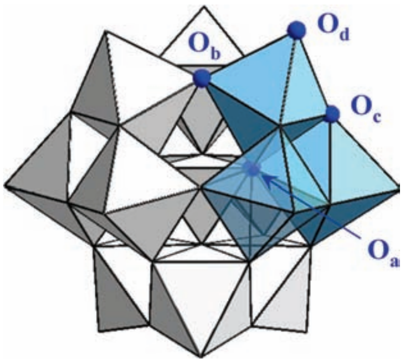

Figure 1. Polyhedral representation of the Keggin-type polyoxometalate and its four different oxygen atoms.

activation is usually achieved by replacing Mo(VI) or W(VI) by lower valent metals. Keggin,[17] Dawson,[18] and Lindqvist-type[19] polyoxometalates form stable adducts with a variety of organometallic cations. A recent example reported in the literature concerns an eight-nickel-capped α-Keggin polyoxoazonickelate.[20] Finke has especially designed such species so as to achieve catalysts precursors. A typical example is $[(1,5\text{-COD})\text{Ir}\cdot\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]^{8-}$.[21]

Finally organometallic cation salts of Keggin-type anion are prepared by reaction of Keggin-type structures with the salts of organometallic complexes. Some examples are reported in the literature mainly based on iridium[22] and rhodium.[23] In this case, the Keggin ion ensures a poor interaction with the metallic center which usually keeps its reactivity.[23] The compound $[\alpha\text{-SiW}_{12}\text{O}_{40}]\ [(\text{CH}_3)_3\text{Sn(DMSO)}_2]_4\cdot 2\text{DMSO}$ which has been obtained by reaction of SnMe_4 with anhydrous $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ in DMSO constitutes a recent X-ray structurally characterized example of organometallic cationic salt of Keggin polyoxoanion.[24]

As far as the organosilyl derivatives of polyoxometalates are concerned, the first example of this kind of compound has been reported by Knoth who obtained the $[\alpha\text{-SiW}_{11}\text{O}_{39}\{\text{O(SiR)}_2\}]^{4-}$ anion by reacting RSiCl_3 with $[\alpha\text{-SiW}_{11}\text{O}_{39}]^{8-}$.[25] Then the synthesis of these compounds has been extended to various R terminal groups, providing a new class of hybrid structures which display interesting properties in medicine,[26] polymerization,[27] and catalysis.[28] In addition, the reactivity of RSiCl_3 with multivacant polyoxometalates was investigated under phase-transfer conditions.[29,30] In the case of a *n*-butyl group, the "capped-structure" anion $[\alpha\text{-A-PW}_9\text{O}_{34}(n\text{BuSiO})_3(\text{Si}n\text{Bu})]^{3-}$ was obtained while a *t*-butyl group yielded the "open-structure" anions $[\alpha\text{-A-PW}_9\text{O}_{34}(t\text{BuSiOH})_3]^{3-}$ and $[\gamma\text{-SiW}_{10}\text{O}_{36}(t\text{BuSiOH})_2]^{3-}$ probably because of steric crowding.[31] Moreover, the reactivity of the $\text{RSi(OR}')_3$ organosiloxane with multivacant heteropolytungstates was investigated by Thouvenot et al. who showed that $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ reacts in presence of hydrochloric acid to give $[\gamma\text{-SiW}_{10}\text{O}_{36}\text{-}\{\text{O(SiR)}_2\}]^{4-}$ and $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{OSiR})_4]^{4-}$. According to the nature of the terminal groups R, the functionalized polyoxometalates can act as cross-linkers used in radical copolymerization.[32]

However, up to now, only the reactivity of organosilyl derivatives with lacunar polyoxometalates has been reported. No article deals with the reactivity of these compounds with non lacunar Keggin structures which could lead either to "capped-structure" species or cation salts of Keggin-type anion. In this article we report the reaction of alkylsilane with anhydrous tungsten-based heteropolyacids. We have chosen to work with anhydrous compounds because they display a higher acidity compared to their hydrated analogues.[33]

Experimental Section

Products and Physicochemical Methods. Phosphotungstic acid $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$ (99.9+%, Aldrich) and silicotungstic acid $\text{H}_4\text{SiW}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$ (99.9+%, Aldrich) were used as received. Anhydrous $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ were obtained by thermal treatment (2 h at 200 °C) under high vacuum (10^{-5} Torr). Diethylmethylsilane Et_2MeSiH (97%, ABCR) was stored under argon and degassed prior to use. Oxygen was dried over 4 Å molecular sieves. All experiments concerning the reactivity of heteropolyacids were carried out by using standard air free methodology in argon filled Vacuum Atmospheres glovebox, on a Schlenk line, or in a Schlenk-type apparatus interfaced to high vacuum line (10^{-5} Torr).

Gas phase analyses were performed on a Hewlett-Packard 5890 series II gas chromatograph equipped with a flame ionization detector and a $\text{KCl/Al}_2\text{O}_3$ on fused silica column (50 m × 0.32 mm) or on a Intersmat IGC 120MB gas chromatograph equipped with a thermal conductivity detector and a molecular sieves column (5 Å; 2 m × 1/8″). Elemental analyses were performed at the CNRS Central Analysis Department of Solaize or at the laboratory ICMUB of the University of Bourgogne at Dijon. Diffuse reflectance Fourier-transformed infrared (DRIFT) spectra were recorded on a Nicolet 6700-FT spectrometer by using a cell equipped with CaF_2 or ZnSe windows, allowing in situ studies. Typically, 32 scans were accumulated for each spectrum (resolution 1 cm^{-1}). Raman spectra of solid samples were recorded with a LabRam HR spectrometer (Jobin Yvon). The laser was focused on the solids with a ×100 objective at a power of 100 μW.

Solution NMR spectra were recorded on an AM-300 Bruker spectrometer. All chemical shifts were measured relative to residual ^{1}H or ^{13}C resonance in the deuterated solvents: D_2O δ 4.79 ppm for ^{1}H; DMSO-d_6 δ 2.50 ppm for ^{1}H, 39.5 ppm for ^{13}C. ^{31}P chemical shifts were measured relative to 85% H_3PO_4 aqueous solution. ^{29}Si chemical shifts are referenced to Me_4Si in DMSO-d_6 using the substitution method.

The ^{1}H MAS, ^{13}C CP-MAS, and ^{31}P MAS NMR spectra were recorded on a Bruker DSX-300 or a Bruker Avance 500 spectrometers equipped with a standard 4 mm double-bearing probehead. The ^{29}Si CP-MAS NMR spectra were recorded on

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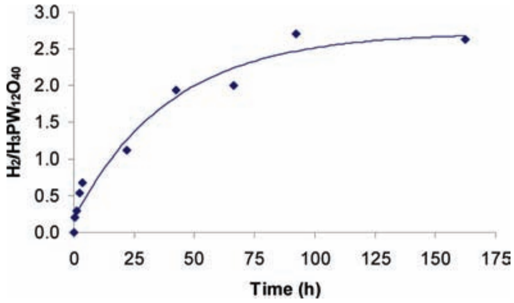

Figure 2. Evolution of hydrogen during the reaction of diethylmethylsilane with anhydrous phosphotungstic acid.

a Bruker DSX-300 spectrometer equipped with a standard 4 mm double-bearing probehead. Samples were introduced under argon in a zirconia rotor, which was then tightly closed. The spinning rate was 10 kHz. A typical cross-polarization sequence was used, with 5 ms contact time and a recycle delay of 1 to 4 s to allow the complete relaxation of the ^1H nuclei. All chemical shifts are given with respect to TMS, as an external reference.

Reaction of Diethymethylsilane with Anhydrous Heteropolyacids in a Batch Reactor. Anhydrous heteropolyacids (typically 3.1×10^{-4} mol) were introduced in a reactor of known volume under strict exclusion of air. An excess of liquid diethylmethylsilane (typically 0.2 mL, $1.4.10^{-3}$ mol) was added without any solvent. The liquid–solid mixture was stirred at room temperature, and the gas phase composition was analyzed by chromatography. When the amount of evolved hydrogen became constant (ca. 48 h) the unreacted silane was removed upon treatment under high vacuum (10^{-5} Torr).

Reactivity of $(Et_2MeSi)_n(XW_{12}O_{40})$ with X = P (n = 3) or Si (n = 4) with Dry Oxygen. The studied sample was loaded in a reactor of known volume under strict exclusion of air. After evacuation of argon, dry oxygen (typically around 100 Torr) was introduced. The system was heated for 12 to 15 h at 100 or 200 °C, and then the oxygen pressure was measured by volumetry to know its consumption. The addition of dry oxygen was done twice.

Results and Discussion

Anhydrous phosphotungstic acid was obtained by thermal treatment (2 h, 200 °C) under high vacuum (10^{-5} Torr) as reported previously.[34] Its ^1H MAS NMR spectrum showed only one relatively broad signal at 8.4 ppm, in agreement with literature data.[35] It was then introduced in a reactor of known volume under strict exclusion of air, and an excess of liquid diethylmethylsilane was added without any solvent. The liquid–solid mixture was stirred at room temperature, and the gas phase composition was analyzed by chromatography as a function of time. As soon as the anhydrous heteropolyacid and the silane were put together, gas analysis showed the evolution of hydrogen. Its amount increased with time and remained quite constant after about 100 h (Figure 2). Whatever the excess of silane introduced into the reactor, quantification of the gas phase showed that about 2.6 equiv of hydrogen per heteropolyacid were released. It should also be pointed out that no methane or ethane was observed in the gas phase.

After completion of the reaction the residual excess of diethylmethylsilane was removed by evacuation under vacuum at room temperature and trapped with liquid nitrogen. ^1H, ^{13}C, and ^{29}Si liquid state NMR spectra confirmed the presence of only the starting silane in the removed product. The solid obtained after this purification step did not contain any physisorbed silane and was then characterized by various physicochemical methods including infrared and Raman spectroscopies and NMR.

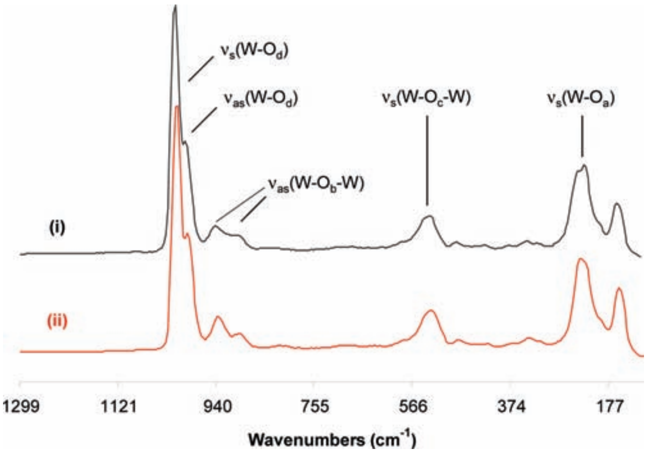

Figure 3. Raman spectra of (i) anhydrous $H_3PW_{12}O_{40}$; (ii) the solid obtained after reaction of $H_3PW_{12}O_{40}$ with Et_2MeSiH and desorption under vacuum (10^{-5} Torr, 1 h, 25 °C).

The Raman spectrum of the obtained powder is shown in Figure 3 together with that of anhydrous $H_3PW_{12}O_{40}$. The anhydrous heteropolyacid shows bands at 1017, 995, 936, 892, 528, and 225 cm^{-1} which were assigned according to the literature data to $\nu_s(W-O_d)$, $\nu_{as}(W-O_d)$, $\nu_{as}(P-O_a)$, $\nu_{as}(W-O_b-W)$, $\nu_s(W-O_c-W)$, and $\nu_s(W-O_a)$, respectively, in agreement with the literature data.[36,37] After reaction with Et_2MeSiH, the spectrum shows quite the same bands. Only a 4 cm^{-1} small shift is observed for the bands involving terminal oxygens (1013 and 991 cm^{-1}, respectively) which could correspond to a small interaction with the organic moiety. We can then conclude from these data that the Keggin structure has been kept after reaction with the silane.

Chemical analyses (%W = 67.7 ± 0.5%; %P = 1.1 ± 0.3%; %C = 1.1 ± 0.3%, and %Si = 1.5 ± 0.3%) are in agreement with a conservation of the Keggin unit and of the $SiEt_2Me$ moiety but because of the errors these data are not a proof as they could also correspond to other species.

Figure 4 shows the DRIFT-IR spectra (in the 1200–4000 cm^{-1} range) of the starting anhydrous $H_3PW_{12}O_{40}$, of Et_2MeSiH and of the solid obtained after reaction. The spectrum of the anhydrous phosphotungstic acid shows only broad bands near 3000 cm^{-1} and 2000 cm^{-1} because of the $\nu(O-H)$ and $\delta(O-H)$ vibrations of the heteropolyacid.[38] Et_2MeSiH shows vibrational bands in the 2955–2874 cm^{-1} and 1457–1234 cm^{-1} regions associated with $\nu(C-H)$ and $\delta(C-H)$, while the intense IR band at 2105 cm^{-1} is characteristic of the $\nu(Si-H)$ vibration. After reaction, the following conclusions can be made: (i) the $\nu(O-H)$ bands have strongly decreased (as the reaction proceeded between a solid and a liquid some intact polyacid remained probably at the

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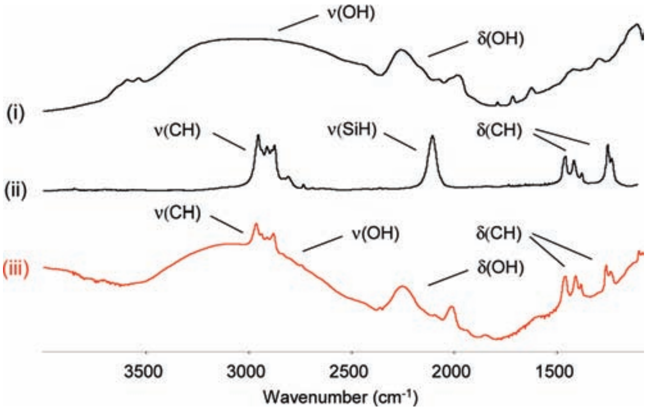

Figure 4. Infrared spectra of: (i) anhydrous $H_3PW_{12}O_{40}$; (ii) Et_2MeSiH on NaCl pellets; (iii) the solid obtained after reaction of $H_3PW_{12}O_{40}$ with Et_2MeSiH and desorption under vacuum (10^{-5} Torr, 1 h, 25 °C).

end of the reaction, in agreement with a 2.6 molecules of hydrogen evolved per Keggin unit); (ii) new bands corresponding to ν(C−H) and δ(C−H) vibrations appeared in the 2960−2876 cm^{-1} and 1460−1236 cm^{-1} ranges, respectively. These two groups of bands have quite the same shapes than those of the starting silane Et_2MeSiH; (iii) and more interestingly, no ν(Si−H) band is observed on the solid, showing that the hydrogen release was due to a reaction of this hydride with the acidic protons of the polyacid. The absence of methane or ethane in the gas phase proves also that no Si−C bond was cleaved and that the above reaction is very clean.

The ^1H solid-state MAS NMR spectrum of the solid recorded under quantitative conditions (with a sufficient delay between two consecutive scans) exhibits two relatively broad signals at 8.4 and 0.3 ppm (Supporting Information, Figure S1). The small resonance at 8.4 ppm was assigned to the acidic protons of some remaining anhydrous phosphotungstic acid[34] confirming that the reaction was not complete, as already suggested by infrared data. In addition, the deconvolution of the NMR spectrum indicated that this resonance corresponded to only about 2% of the total signal. The broad resonance centered at about 0 ppm was ascribed to the protons of both Si−Et and Si−Me groups by comparison with data on related compounds (for example, in Et_2MeSiH the protons of Si-Me give a peak at 0.02 ppm and those of Si-Et two peaks at 0.56 and 0.96 ppm). No signal ascribed to the Si−H moiety (expected around 4 ppm) could be observed, in agreement with infrared data and with a reaction involving this hydride and leading to a cleavage of the Si−H bond.

The solid-state ^{13}C CP-MAS NMR of the obtained solid shows two resonances at −4.1 and +6.6 ppm. However, the deconvolution of the spectrum shows that the signal at +6.6 ppm is the sum of two components at +6.3 and +8.1 ppm (Figure 5). Comparison of these chemical shifts to the values found in the literature (Table 1) allows to suggest that the resonance at −4.1 ppm corresponds to the Si−CH_3 group while those at +6.3 and +8.1 ppm can be attributed to a Si−CH_2−CH_3 species. Solid-state NMR is then in agreement with a reaction involving only the Si−H bond while the −$SiMeEt_2$ group remains unchanged.

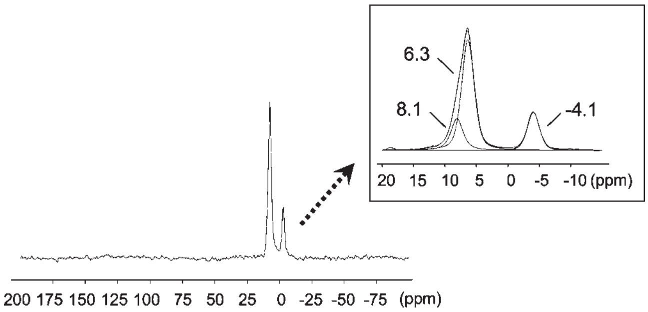

Figure 5. ^{13}C CP-MAS NMR spectrum of the solid obtained after reaction of anhydrous $H_3PW_{12}O_{40}$ with Et_2MeSiH followed by desorption under vacuum (10^{-5} Torr, 1 h, 25 °C).

Table 1. ^{13}C Chemical Shifts for Some Alkyl and Chlororoalkylsilane Compounds

compound	Si−$\mathbf{CH_3}$	Si−$\mathbf{CH_2}$−CH_3	Si−CH_2−$\mathbf{CH_3}$
Me_3SiH	−4.6		
Et_3SiH		8.2	2.6
Et_2MeSiH	−7.2	4.2	7.9
Me_2SiHCl	1.3		
$Me(EtO)_2SiH$	−3.1		
$Me(MeO)_2SiH$	−3.9		
Me_3SiCl	3.3		
Et_3SiCl		4.6	6.7
$Et_2MeSiCl$	−1.9	7.1	6.4
$[Et_2MeSi]_3PW_{12}O_{40}$	−4.1	6.3	8.1

Solid-state ^{31}P MAS NMR can provide informations about the structure of the polyoxometalate and more precisely if there is a mixture after reaction. The spectrum (Supporting Information, Figure S2) displays two signals at −12.0 and −16.7 ppm. The first peak, corresponding to less than 10% of the total signal, can be assigned to residual anhydrous $H_3PW_{12}O_{40}$ which had not reacted, in agreement with literature[35] and the above data. The resonance at −16.7 ppm is then ascribed to the species obtained after reaction. The presence of only two peaks is quite important as it shows the presence of only two species, one of them being the unreacted polyacid and the other one being obtained after a complete reaction of the three protons around the polyanion. There is no formation of mixed compounds where only part of the protons had reacted. However, at this stage, no information about the interaction between the Keggin unit and the -$SiMeEt_2$ group can be deduced from these results.

More interesting results about the silicon nuclei environment can be obtained by using solid-state ^{29}Si CP-MAS NMR and could allow to elucidate the interaction between the organic and inorganic moieties. The ^{29}Si CP-MAS NMR spectrum of the solid (Figure 6) displays two peaks at +61 and +57 ppm. These values are quite unusual for silicon coordinated to carbon and oxygen (in a first approximation the polyoxometalate can be considered as a bowl covered by oxygen atoms). In organometallic chemistry some examples are found for mercury, cadmium, or iron compounds displaying a metal−silicon bond (Table 2). In that case the high values of the ^{29}Si NMR chemical shifts were attributed to interactions between the two nuclei involving low-lying mercury or cadmium orbitals, resulting in bonds considerably shorter than the sum of the covalent radii.[39] Such an explanation is not acceptable in our case as the only one metal, tungsten, is not accessible and the polyoxometalate is not reduced (as evidenced by the absence of blue color of the resulting solids and by oxygen consumption, see below). Another family of compounds which display high chemical

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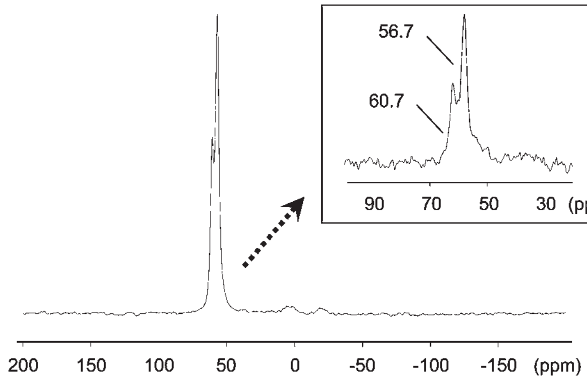

Figure 6. ^{29}Si CP-MAS NMR spectrum of the solid obtained after reaction of anhydrous $H_3PW_{12}O_{40}$ with Et_2MeSiH followed by desorption under vacuum (10^{-5} Torr, 1 h, 25 °C).

Table 2. ^{29}Si Chemical Shifts for Some Organic and Organometallic Compounds Containing Silicon

entry	compound	δ_{Si} (ppm)	ref.
1	Et_2MeSiH	−6.2	44
2	Et_3SiH	0.2	44
3	Me_3SiH	−15.5	44
4	$Me_3Si\text{-}SiMe_3$	−19.6	44
5	$Et_3Si\text{-}SiEt_3$	−9.4	44
6	$(MeO)_3Si\text{-}Si(OMe)_3$	−52.5	44
7	Me_3SiOMe	17.2	44
8	$Me_2Si(OMe)_2$	−2.5	44
9	$MeSi(OMe)_3$	−41.4	44
10	$Si(OMe)_4$	−79.2	44
11	$Me_3SiHg\underline{\mathbf{Si}}H_3$	−22.1	45
	$Me_3\underline{\mathbf{Si}}HgSiH_3$	63.7	45
12	$Me_3SiSnMe_3$	−11.0	46
13	$MeHgSiMe_3$	33.0	39
14	tBuHgSiMe$_3$	33.6	39
15	$\{[PhC(N\textit{t}Bu)_2]SiO\textit{t}Bu\}Fe(CO)_4$	40.3	47
16	$Me_3SiHgGeH_3$	41.1	45
17	$(\textit{t}Bu_3Si)_2Cd$	47.5	44
18	$(Et_3Si)_2Hg$	50.2	44
19	$(Me_3Si)_2Hg$	63.6: 64.0	39,45
20	$(Me_3SiOEt_2)^+(TFPB)^-$	66.9	48
21	$\textit{i}Pr_3Si[B(C_6F_5)_4]$	94.0	42

shifts is that where silicon is weakly interacting with another element and has a positive charge, for example, in $\textit{i}Pr_3Si[B(C_6F_5)_4]$ for which the ^{29}Si NMR chemical shift is +94.0 ppm (Table 2). Indeed, the polyoxometalate in its acid form is known to display highly acidic properties (stronger than sulfuric acid), and its conjugated base, the polyanion, is thus a very bad nucleophile. As a consequence, the Si−O bond between the silicon and the oxygen atom of the polyoxometalate should not be strong and could explain the deshielding of silicon, exactly as we observed it previously for the grafting reaction of tetramethyl tin on H−Y zeolite (a highly acidic support for the cracking of alkanes) for which the ^{119}Sn MAS NMR chemical shift was also deshielded compared to that usually observed on "neutral" supports such as silica (+260 ppm instead of +100 ppm).[40]

To confirm this hypothesis we have performed a series of calculations on $Et_2MeSi\text{-}OCH_3$ with optimization of the structure and calculation of the NMR chemical shifts as a function of the Si−O distance. These calculations show that (i) the ^{29}Si NMR chemical shift is greatly dependent on the Si−O distance (Figure 7) while (ii) the ^{13}C NMR shifts do not vary significantly whatever the Si−O distance (Supporting Information, Table S3), in agreement with the experimental results. The observed chemical shift should correspond to an increase of the Si−O distance of 0.2 nm compared to that achieved in the optimized structure. These calculations, even if they were made at a relatively low level of theory (B3LYP/6-31+G* with a calculation of the chemical shifts by use of the GIAO method) are however relatively accurate as the value obtained for the isolated cation Et_2MeSi^+ is 374 ppm in good agreement with the values obtained by more sophisticated methods.[41]

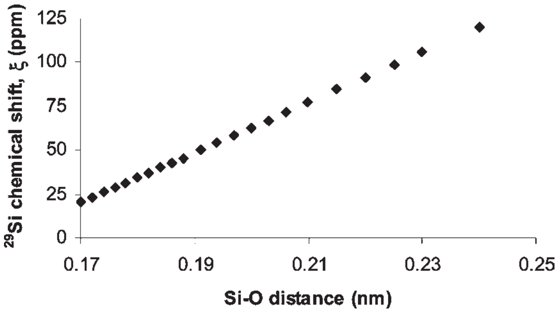

Figure 7. Theoretical ^{29}Si NMR chemical shifts of $Et_2MeSi\text{-}OCH_3$ as a function of the Si−O distance.

These calculations are then in agreement with a weak Si−O bond in the solid which can then be written formally as $(Et_2MeSi)_3(PW_{12}O_{40})$, on the basis of all above results. The presence of two peaks in the ^{29}Si CP-MAS NMR spectrum can be interpreted by the presence of two different kinds of Si−O interactions between the alkylsilane moiety and the Keggin unit. Even if a cross-polarization sequence is not quantitative, one can reasonably suppose that the two species are Et_2MeSi groups interacting with different oxygen atoms of the polyoxometalate and so that they are very similar chemically and should display quite the same behavior from the point of view of the polarization transfer from protons to silicon. In these conditions the relative intensities of the two peaks (1:2) should reflect the relative proportions of the two species. This ratio could be explained by the two types of oxygen atoms in the Keggin structure. Indeed there are 12 terminal oxygens and 24 sterically accessible bridging oxygens which correspond to a ratio 1:2. The signal at 60.7 ppm could then be assigned to $[Et_2MeSi]$ groups in interaction with terminal oxygens of the polyoxometalate while the resonance at 56.7 ppm could be ascribed to a silane group in interaction with bridging oxygen atoms.

To determine if this reaction was general or only specific of the phosphotungstic acid, other heteropolyacids were also used. In the case of molybdic heteropolyacids the situation is rather more complicated and will be described elsewhere

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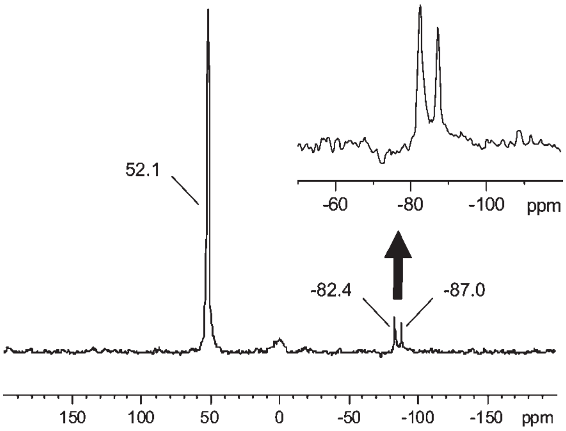

Figure 8. ^{29}Si CP-MAS NMR spectrum of the solid obtained after reaction of anhydrous $H_4SiW_{12}O_{40}$ with Et_2MeSiH followed by desorption under vacuum (10^{-5} Torr, 1 h, 25 °C).

but for the silicotungstic acid quite the same behavior was observed. However, the amount of hydrogen released was lower than the expected value, with 1.7 equiv for $H_4SiW_{12}O_{40}$ (while a complete reaction should lead to 4 equiv of hydrogen). All other characterizations led to similar conclusions than those obtained in the case of phosphotungstic acid. For example the ^{1}H MAS NMR spectrum (Supporting Information, Figure S3) is quite comparable to the one obtained above with only two signals around 8 and 0 ppm, but the relative intensity corresponding to the acidic protons at about 8 ppm is higher. As above, the signal of the Si−H proton is absent. The solid state ^{29}Si CP-MAS NMR spectrum of the species prepared with $H_4SiW_{12}O_{40}$ displays three resonances at 52.1, −82.4, and −87.0 ppm (Figure 8). The signal at 52.1 ppm belongs to the same unusual range of chemical shifts previously discussed for $H_3PW_{12}O_{40}$. However, there is in this case only one unusual resonance which was assigned to a single Si−O interaction. It is therefore not possible to distinguish the two kinds of oxygen atoms (bridging or terminal). The two other peaks correspond to the central atoms of the Keggin unit: the resonance at −87.0 ppm was assigned to the species obtained after reaction while the peak at −82.4 ppm corresponds to anhydrous silicotungstic acid which has not reacted. A key point when looking at the resonance of the silicon atom of the Keggin structure is that there are two species and only two species, as already observed for phosphotungstic acid, one unreacted and one which has reacted. As a consequence here also there is not a mixture of $(Et_2MeSi)_{4-x}H_xSiW_{12}O_{40}$ species, with $x = 0$ to 4, as it can be expected from a partial consumption of the acidic protons, but only two compounds, one of them being the unreacted polyacid. Consequently, we can propose that, as for the phosphotungstic acid, the reaction is probably complete when the protons are accessible and the fact that all protons did not react is related to kinetics. One can reasonably imagine that the reaction proceeds through diffusion of Et_2MeSiH through the polyacid which has reacted. This diffusion is probably slower in the case of silicotungstic than in that of phosphotungstic acid.

Additional proofs for a weak interaction between the silane and the polyoxometalate can be obtained by studying chemical reactions of this new species. For example, if there is a ionic-type bond between the organic and inorganic moieties, it should be possible to deplace it by reaction with another salt. We then studied the reaction of $(Et_2MeSi)_3(PW_{12}O_{40})$ with tetrabutylammonium chloride. For this purpose the solid was first dissolved in dimethyl sulfoxide (DMSO), and its ^{29}Si NMR spectrum was recorded (Supporting Information, Figure S4). The spectrum shows only one relatively broad peak at 41.1 ppm, a value less deshielded than in the solid state but which is still unusual for a silicon atom. The difference of chemical shifts between liquid- and solid-state NMR spectra (ca. 15−20 ppm) can be explained by the coordination of the solvent to the silicon atom assuming a shortening of the interaction. This phenomenon is similar to what has been recently reported in the literature for the $[SnMe_3(DMSO)_2]^+$ trialkyl tin salts of polyoxometalates.[24] The broadening of the peak could be due to exchange phenomena. This attribution is also proved by ab initio calculations of the $[Et_2MeSi(DMSO)]^+$ cation which led to a value of 70.9 ppm for the ^{29}Si NMR chemical shift (Supporting Information, Table S2). This value is also in full agreement with ^{29}Si resonances observed for $[R_3Si(Solvent)]^+$ cations.[42,43]

When tetrabutylammonium chloride was added, the ^{29}Si NMR signal disappeared completely. However a careful observation of the NMR tube showed the presence of two phases which were separated and analyzed. The lower phase (which corresponded to most of the liquid) contained only the polyoxometalate as its tetrabutylammonium salt as shown by ^{31}P and ^{13}C NMR while the small upper phase (resolubilized in C_6D_6) did not show any signal in ^{31}P NMR but three peaks at 8.2, 6.7, and −2.6 ppm in ^{13}C NMR. By comparison with literature data these signals can be attributed to diethylmethylchlorosilane. This result indicates clearly that an exchange of the alkylsilane moiety occurred: in presence of the quaternary ammonium salt, the Si−O bond was cleaved and led as a consequence to a classical quaternary ammonium salt of the polyoxometalate and to the release of $Et_2MeSiCl$ which was not soluble in the DMSO phase.

$$(Et_2MeSi)_3(PW_{12}O_{40}) + 3n\mathrm{Bu_4NCl}$$
$$\rightarrow (n\mathrm{Bu_4N^+})_3(PW_{12}O_{40}{}^{3-}) + 3Et_2MeSiCl$$

This reactivity strengthens the hypothesis that the interaction between the alkylsilane moiety and the anhydrous heteropolyacid is weak, leading to a long distance between the silicon atom of the organic moiety and the oxygen atoms of the polyoxometalate.

Such a "Et_2MeSi^+" species should be also reactive toward oxygenated molecules. We have therefore studied its reactivity with molecular oxygen (preliminary dried). At room temperature, no oxygen consumption was observed, while after heating at 100 °C about one oxygen molecule was consumed per Keggin unit and more than two oxygen molecules after heating at 200 °C. The ^{29}Si CP-MAS NMR spectrum of the sample $(Et_2MeSi)_3(PW_{12}O_{40})_{/\mathrm{Add.\ O2}}$ heated under oxygen at 200 °C is shown in Figure 9. The ^{29}Si NMR resonances of "Et_2MeSi^+" at 60.7 and 56.7 ppm disappeared and have been replaced by two broad resonances at −55 and −98 ppm. On the basis of literature data, these peaks were attributed to T and Q species. Note that as the spectrum was recorded by use of a cross-polarization sequence, the relative intensities of both species do probably not reflect their relative amounts (in contrast to the above case where the two compounds were chemically equivalent). Nevertheless these data show unambiguously

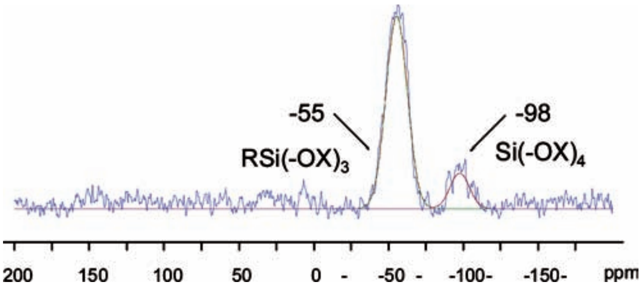

Figure 9. ^{29}Si CP-MAS NMR spectrum of the solid $(Et_2MeSi)_3$-$(PW_{12}O_{40})_{/Add.\ O2}$ obtained after reaction with dry oxygen at 200 °C.

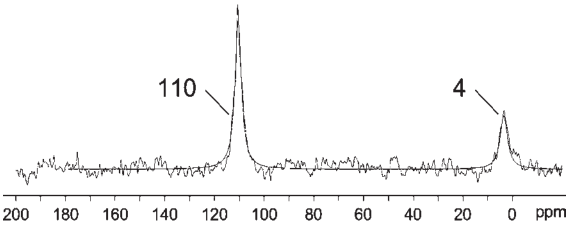

Figure 10. $^{13}C\{^1H\}$ MAS NMR spectrum of the solid $(Et_2MeSi)_3$-$(PW_{12}O_{40})_{/Add.\ O2}$ obtained after reaction with dry oxygen.

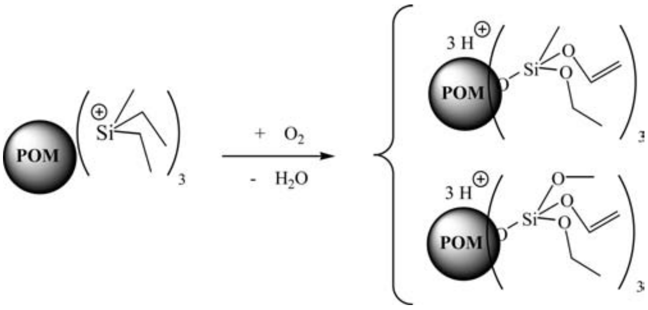

Figure 11. Explanation of the presence of C═C double bond in $(Et_2MeSi)_3(PW_{12}O_{40})_{/Add.\ O2}$ obtained after reaction with dry oxygen.

that at least two Si−C bonds have been replaced by Si−O ones revealing that oxygen atoms have been inserted in the silicon environment. As a consequence, this observation has to be linked to the consumption of dry oxygen.

However, a problem remains concerning the charge compensation as the resulting T $(Si\text{-}O)_3$ or Q $(Si\text{-}O)_4$ units are not charged. To clarify this point, the $^{13}C\{^1H\}$ NMR spectrum of the solid was recorded and is shown in Figure 10. The spectrum exhibits two resonances at 4 and 110 ppm. The peak at 4 ppm corresponds to an alkyl group linked to silicon while the signal at 110 ppm was assigned to an olefinic group. The presence of this kind of carbon atom can explain the charge compensation by the cleavage of a C−H bond and the consecutive formation of a C═C double bond and a proton as depicted in Figure 11.

Conclusion

In conclusion, we have investigated the reactivity of alkylsilane with anhydrous tungsten-based heteropolyacids. This study showed that the polyoxometalates react to give a new class of compounds in which a weak interaction exists between the Keggin-type anion and the resulting organosilyl moiety. Therefore these compounds can be described as an intermediate structure between known species of polyoxometalates including organometallic complexes, especially complexes capped on polyoxometalate and organometallic cation salts of Keggin-type anion. The weakness of the interaction is probed by reaction with tetrabutylammonium chloride and oxygen.

Note that this kind of structure can be of great interest in microelectronics because of the delocalization of charge. Indeed, rather than to use a doping technique to introduce defects in semiconductors such as silicon, this could be done easily by covering the surface with Si−H species and reacting them with polyacids. Depending on both the polyacid and Si−H amounts, the amount of defects introduced in the semiconductor could be tuned easily. In addition the redox properties of the polyoxometalates could give new characteristics to these materials.

Supporting Information Available: Further details are given in Figures S1−S4 and Tables S1−S2. This material is available free of charge via the Internet at http://pubs.acs.org.