

Easily Immobilized Di- and Tetraphosphine Linkers: Rigid Scaffolds that Prevent Interactions of Metal Complexes with Oxide Supports

Yuan Yang,[†] Björn Beele,[†] and Janet Blümel^{*‡}

Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, Texas 77842-3012, and Chemistry Department, University of Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany

Received January 22, 2008; E-mail: bluemel@tamu.edu

Bifunctional phosphine linkers have played a crucial role in developing a molecular chemistry based upon oxide supports. These versatile connecting units have been applied in many areas of chemistry, for example as scavengers for metal complexes, in combinatorial methodologies, and for immobilizing catalysts.¹ Any contact of the latter with reactive oxide surfaces, however, shortens their lifetime. In this contribution, we disclose a new linker system with a rigid tetraphenylelement scaffold, which is easy to synthesize and immobilize and renders any contact of the metal with the oxide surface sterically impossible.

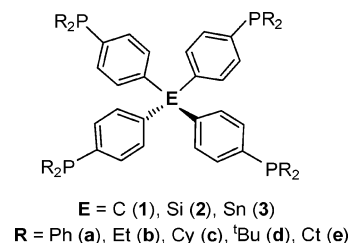
For many years, our group² as well as others³ has studied the grafting of catalysts to oxide supports and the activities and lifetimes of the anchored species. Bifunctional mono- and diphosphine/triethoxysilane systems have commonly been applied,⁴ one example of which is [Ph₂P(CH₂)₇Si(OEt)₂].^{4a} Although catalysts bound through the resulting covalent assemblies can be recycled many times,² an important general problem remains: it is possible for the catalysts to become deactivated via contact with the oxide surface. Especially linkers with flexible alkyl chains allow the phosphine moiety to bend down to the surface. One way to avoid contact of the metal with the surface would be to “passivate” it by covering it with Me₃Si groups⁵ prior to attaching the precatalyst to the surface-bound linker. In practice, however, the success of this method—which furthermore requires an extra step—is limited.

First we considered linkers with tetraarylmethane cores, containing one to three *p*-triethoxysilyl groups in analogy to the bifunctional phosphines of the previous generations,⁴ such as [Ph₂P(*p*-C₆H₄)₃C-(*p*-C₆H₄)Si(OEt)₃] or [Ph₂P(*p*-C₆H₄)C]C[(*p*-C₆H₄)Si(OEt)₃]. Although these syntheses proved feasible, the purification of such large molecules that cannot be chromatographed or crystallized turned out to be rather tedious. We therefore developed an alternative, more convenient methodology.

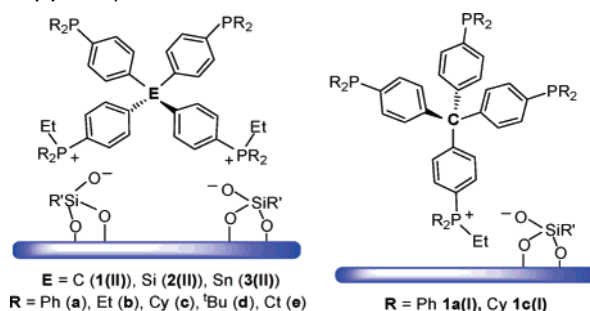
We first synthesized a variety of new tetraphosphine compounds with tetraphenylmethane (1),^{6a} -silane (2),^{6b} and -stannane (3)^{6c} cores. As summarized in Scheme 1,⁶ numerous phosphine substituents can be introduced, giving the compounds **1a–d**, **2a–e**, and **3a,b,e**. The series **1a–d** was prepared by tetralithiation of C[(*p*-C₆H₄)Br]₄⁷ with excess ⁿBuLi at –78 °C⁸ and quenching with the corresponding chlorophosphines ClPR₂. For the silanes **2** and stannanes **3**, we explored two different routes. Following the monolithiation of *p*-dibromobenzene or *p*-bromoiodobenzene, addition of SiCl₄ or SnCl₄ gave tetrabromotetraphenylsilane^{7a} or -stannane.^{6c} These were subsequently transformed into **2a–d** and **3a,b,e** by analogy to **1a–d**. Alternatively, the Grignard reagent derived from Ph₂P(*p*-C₆H₄Br)^{8b} gave **2a** and **3a** after reaction with SiCl₄ and SnCl₄. All of the preceding compounds have been characterized by standard analytical techniques.

Next we explored the immobilization of tetraphosphines **1–3**. It is known since our early work⁹ that even phosphines without

Scheme 1. Tetraphosphines with Rigid Tetraphenylelement Scaffold⁶



Scheme 2. Tetraphosphines Immobilized on Silica via One (I) and Two (II) Phosphonium Moieties



intramolecular ethoxysilane function can be irreversibly bound on silica¹⁰ by adding Cl(CH₂)₃Si(OEt)₃ and stirring the mixture a few hours at 80 °C. More recently we could determine the nature of the surface linkage and prove with solid-state NMR that ethylphosphonium cations are formed, which are bound to surface siloxide anions.^{9b} For catalyst immobilization this mode does not work with monophosphines, or diphosphines that are connected via flexible spacers, since both lone pairs would be ethylated.

However, tetraphosphine linkers of the type in Scheme 1, with rigid tetrahedral geometries should—even if three of the lone pairs were to be ethylated—always retain at least one Lewis basic binding site.

When phosphines **1–3** are treated with an excess of (EtO)₃Si-(CH₂)₃Cl (**4**) in the presence of silica, the surface-bound diphosphonium species (II), depicted in Scheme 2 (left), results. This is proven by the ³¹P solid-state NMR spectra (Figure 1, Table 1). The top trace in Figure 1 presents the ³¹P CP/MAS¹¹ spectrum of **1a(II)**. Besides the resonance for the phosphonium moieties at 23.0 ppm, there is still a signal for nonquaternized phosphines at –6.2 ppm. Both signals have the line widths and chemical shift anisotropies (CSA) typical for their compound classes.^{9b} Measuring with CP¹¹ does not give the correct integrals, however, because the nucleus with more nearby aliphatic protons, in this case the ethylphosphonium ³¹P nucleus, profits more from the magnetization transfer ¹H-³¹P and thus gives the more intense line. Therefore, a ³¹P experiment with MAS and simple high-power decoupling

[‡] Texas A&M University.

[†] University of Heidelberg.

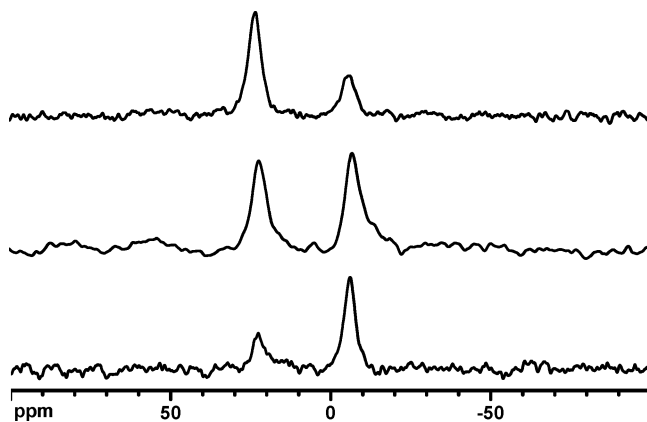


Figure 1. ^{31}P CP/MAS NMR spectra of **1a(II)** (top trace) and **1a(I)** (middle). Bottom trace: ^{31}P MAS of **1a(I)**. Rotational frequency 4 kHz.

Table 1. ^{31}P CP/MAS Chemical Shifts of the Di- and Tetraphosphines Attached by One (I) and Two (II) Phosphonium Moieties and the $\delta(^{31}\text{P})$ of the Molecular Species in Solution (C_6D_6)

	$\delta(^{31}\text{P})$ of $[\text{R}'\text{PR}_2\text{Et}]^+$ groups	$\delta(^{31}\text{P})$ of $\text{R}'\text{PR}_2$ groups	$\delta(^{31}\text{P})$ of phosphines in C_6D_6
1a(I)	22.5	-6.1	-6.52
1a(II)	23.0	-6.2	-6.52
1b(II)	32.1	-16.3	-17.56
1c(I)	29.3	1.0	0.78
1c(II)	29.6	1.1	0.78
1d(0)	39.1	29.1	26.42
2a(II)	23.9	-4.6	-5.27
2b(II)	33.9	-15.2	-16.17
2c(II)	30.6	1.6	3.47
2d(II)	34.4	39.9	38.95
2e(II)	33.4	2.2	1.30
3a(II)	24.0	-5.0	-5.23
3b(II)	33.6	-16.8	-17.38
3e(II)	33.5	1.90	1.41
5(I)	22.4	-3.9	-5.48
6(I)	21.6	-6.0	-5.96

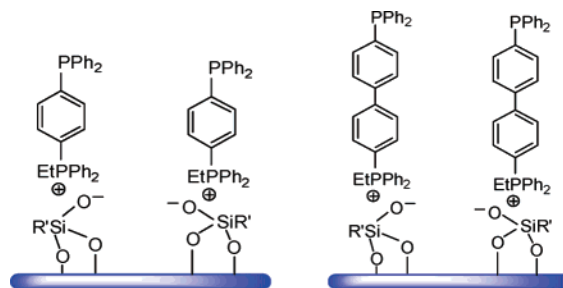
together with a long relaxation delay was applied, which gave a 1:1 signal intensity ratio.

In order to explore the scope of this method, we varied the substituents R at the phosphine moieties according to Scheme 1. All tetraphosphines could be immobilized by the phosphonium method in the same way and gave ^{31}P resonances in the expected narrow range (Table 1).^{9b} Interestingly, this kind of immobilization also works with dried alumina as the support.

Among the various silane reagents we tested for this immobilization, $\text{HSi}(\text{OEt})_3$ and **4** were the most efficient. It should be mentioned that **4** does not quaternize any of the tetraphosphines even at elevated temperatures in solution without silica. $\text{Me}_2\text{Si}(\text{OEt})_2$ afforded only minor amounts, and Me_3SiOEt none of the surface-bound phosphonium species. Therefore, we assume that the siloxide counteranion does not stem from the silica support itself but rather from the ethoxysilanes bound to the surface. In the case of surface-bound Me_3SiOEt there is no ethoxy group left at the silane that could function in this way. This is corroborated by the fact that silica modified with ethoxy groups by refluxing in EtOH ^{5a} did not bind phosphines on its surface.

Next we tested whether the reaction sequence used for immobilization was important. For this purpose, the silica surface was first modified with the maximal number of about 72 molecules of **4** per 100 nm^2 , according to the standard procedure.^{5b} An excess of the phosphine **1a** was added to the modified silica, and the suspension was stirred in toluene at $90\text{ }^\circ\text{C}$. The resulting material (surface coverage typically four molecules per 100 nm^2) gave a

Scheme 3. Diphosphines **5** and **6** Immobilized on Silica via One Phosphonium Moiety to Give **5(I)** and **6(I)**



^{31}P CP/MAS spectrum identical to that shown in Figure 1 (top trace).

This finding suggested a means of quaternizing selectively only one of the phosphine moieties of the tetraphosphines. Accordingly, silica was modified with a minor amount of **4** (1.8 particles per 100 nm^2), such that the surface dilution of **4** would lead to an average silicon–silicon distance much greater than the phosphorus–phosphorus distance in **1**. Subsequent addition of **1a** or **1c** gave a material, where only one phosphine out of the four was quaternized, forming **1a(I)** or **1c(I)** (Scheme 2, right) with a surface coverage of typically 1.5 molecules per 100 nm^2 . Figure 1 shows the ^{31}P CP/MAS spectrum (middle trace) and the ^{31}P MAS spectrum without CP (bottom). Like in the previous case, the measurement done with high-power decoupling only represented the true 1:3 intensity ratio better than the CP spectrum, which enhances mostly the intensity of the ethylphosphonium ^{31}P signal due to the alkyl protons close to the phosphorus nucleus.¹¹

In order to provide additional evidence that in the case of species **II** the signal intensities are not composed by a distribution of molecules bound by one, two, and three phosphonium groups, with the same amounts of the first and the latter, we turned to other simple model systems. Instead of the above tetraphosphines the diphosphines $\text{Ph}_2\text{P}(p\text{-C}_6\text{H}_4)\text{PPh}_2$ (**5**) and $\text{Ph}_2\text{P}(p\text{-C}_6\text{H}_4)_2\text{PPh}_2$ (**6**) with rigid phenyl and biphenyl backbones^{8a} were employed. Due to steric reasons in these cases too, only one phosphine moiety per molecule was bound as a phosphonium group, while the other one remained unquaternized (Scheme 3).

The ^{31}P chemical shifts of **5(I)** and **6(I)** are very similar to those of the surface-bound tetraphosphines (Figure 2, Table 1). The correct signal intensities of 1:1 are obtained with simple high-power decoupling, as shown for **5(I)** in Figure 2 (bottom). With a short contact time of 1 ms CP enhances the phosphonium ^{31}P signal as compared to the triarylphosphine moiety with the same factor as in the cases of the immobilized tetraphosphines (Figure 2, middle).

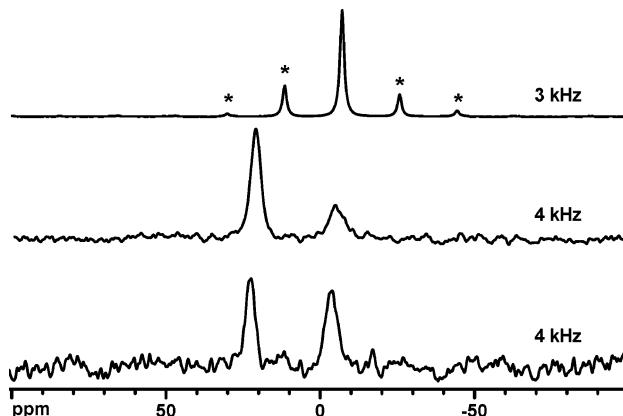


Figure 2. ^{31}P CP/MAS spectra of polycrystalline **5** (top) and **5(I)** (middle) and ^{31}P MAS (bottom) of **5(I)**. *rotational sidebands.

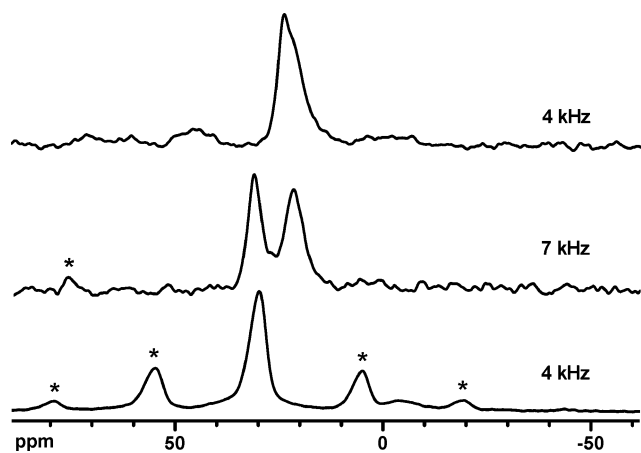


Figure 3. ^{31}P CP/MAS NMR spectra of $[\mathbf{1a}(\text{II})\text{Et}_2]^{2+}\cdot 2\text{BF}_4^-$ (top trace), $\mathbf{1a}(\text{II})(\text{AuCl})_2$ (middle), and $\mathbf{1a}(\text{AuCl})_4$ (bottom). *rotational sidebands.

However, using longer contact times of up to 12 ms increases the triarylphosphine signal intensity as expected,¹¹ with a 3:2 ratio of ethylphosphonium to phosphine signal intensity. Regarding the ^{31}P CP/MAS signal of polycrystalline **5** with its large CSA and small residual line width (Figure 2, top), it is also clear that the spectrum of **5(I)** cannot result from a composition of species bound by two phosphonium groups and residual polycrystalline material. The latter would furthermore have been washed off with the solvent.

The phosphonium salts presented here are bound irreversibly to the support as long as the latter is not dissolved. Even the usual ion exchange methods, e.g., treating the modified silica with acids, bases, or other soluble counterions, did not remove even traces of phosphine species, as established by ^{31}P NMR of the supernatant solution. After these treatments the spectra in Figures 1 and 2 were unchanged. Hence, the phosphonium linkages are even more robust with respect to leaching^{12a} or decomposition^{12b} than ethoxysilane linkers.^{12a} Siloxide anions seem to be the most firmly bound counterions, and consequently phosphonium salts such as $[\text{Ph}_3\text{PEt}]\text{-Br}$ can be irreversibly bound to silica by simply stirring the latter with a solution of the phosphonium salt in toluene.

Finally, we sought to demonstrate that the remaining phosphine groups of the immobilized linkers could be derivatized. Accordingly, **1a(II)** was treated with $[\text{Et}_3\text{O}]\text{BF}_4$ in ether at ambient temperature. The ^{31}P CP/MAS (Figure 3, top) showed only a single signal, consistent with the formation of the surface-bound tetraphosphonium cation $[\mathbf{1a}(\text{II})\text{Et}_2]^{2+}\cdot 2\text{BF}_4^-$. Complexation of **1a(I)** using AuCl (THT) cleanly gave **1a(I)(AuCl)₃**, as evidenced by the disappearance of the phosphine resonance in the ^{31}P CP/MAS spectrum, and the appearance of a new signal, comparable to the one of the polycrystalline **1a(AuCl)₄** (Figure 3, bottom) with respect to the chemical shift and shift anisotropy at 32.2 ppm (Figure 3, middle). These results show that the immobilized linker is rather robust and that the remaining phosphine groups can be derivatized in a variety of ways.

In conclusion, we have demonstrated that di- and tetraphosphines with rigid backbones can be easily synthesized and immobilized irreversibly via an ionic bond as phosphonium salts ad libitum with one or two binding sites. This way of binding does not require an intramolecular ethoxysilane functionality, making major synthesis and purification efforts obsolete. Depending on the phosphine type and the immobilization procedure chosen, one, two, or three free phosphine groups per molecule remain. These can be used for example for coordinating catalysts, which we will explore in more detail in the future.

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- Representative syntheses and data: (a) **1d**: 2 mL of a 1.6 M solution of $^n\text{BuLi}$ (3.220 mmol) in hexane was added dropwise to a solution of 256 mg (0.402 mmol) of $\text{C}(p\text{-C}_6\text{H}_4\text{Br})_4$ in 150 mL of ether at -78°C . Then, the mixture was brought to ambient temperature over 2.5 h, during which time a white suspension formed. After the mixture was cooled to -78°C , CIPBu_2 (0.61 mL, 3.220 mmol) was added, and the mixture was slowly warmed to room temperature. After the mixture was stirred overnight and the solids were filtered off, the solvent was removed in vacuo. **1d** could be obtained as a colorless powder and purified by recrystallization from toluene/ethanol (1:5) (186 mg, 51.6% yield). ^1H NMR (C_6D_6): $\delta = 7.64$ (dd, $^3J(\text{H-H}) = 8.2$ Hz, $^3J(\text{P-H}) = 6.0$ Hz, 8H; PCCH), 7.38 (d, $^3J(\text{H-H}) = 8.2$ Hz, 8H; PCCHCH), 1.20 (d, $^2J(\text{P-C}) = 11.4$ Hz, 72H; CH_3) ppm; ^{13}C NMR (C_6D_6): $\delta = 136.04$ (d, $^2J(\text{P-C}) = 23.0$ Hz; PCCH), 135.47 (d, $^1J(\text{P-C}) = 25.2$ Hz; PCCH), 130.29 (d, $^3J(\text{P-C}) = 8.2$ Hz; PCCHCH), 147.09 (s, PCCHCHC), 65.33 (s, $(\text{C}_6\text{H}_4)_4\text{C}$), 31.69 (d, $^1J(\text{P-C}) = 23.2$ Hz; CCH_3), 30.36 (d, $^2J(\text{P-C}) = 14.9$ Hz; CH_3) ppm; ^{31}P NMR (C_6D_6 , 121.5 MHz): $\delta = 26.42$ ppm. HR-MS (FAB⁺): $[\text{M}]^+$ (100.0%) 897.2048 (calcd. 897.2037). (b) **2b**: A 1.6 M solution of $^n\text{BuLi}$ (0.77 mL, 1.23 mmol) in hexane was added dropwise to 100 mg (0.15 mmol) of $\text{Si}(p\text{-C}_6\text{H}_4\text{Br})_2$ in 70 mL of ether at -78°C . The solution was warmed up to ambient temperature in the course of 2.5 h. Then, it was cooled down to -78°C , and 0.16 mL (1.84 mmol) of CIPET₂ was added. After having been warmed to room temperature and stirred overnight the solvents were removed in vacuo, and the product was extracted with CH_2Cl_2 . **2b** (71 mg, 0.1 mmol) was obtained as a colorless waxy material (mp 72°C) after removal of the solvent, corresponding to a yield of 66.7%. ^1H NMR (C_6D_6): $\delta = 7.69$ (dd, $^3J(\text{H-H}) = 8.0$ Hz, $^4J(\text{P-H}) = 0.9$ Hz, 8H; PCCHCH), 7.45 (dd, $^3J(\text{H-H}) = 7.9$ Hz, $^3J(\text{P-H}) = 6.6$ Hz, 8H; PCCH), 1.51 (m, 16H; PCH_2), 0.97 (t, $^3J(\text{H-H}) = 7.6$ Hz, 12H; CH_3), 0.93 (t, $^3J(\text{H-H}) = 7.6$ Hz, 12H; CH_3) ppm; ^{13}C NMR (C_6D_6): $\delta = 141.84$ (d, $^1J(\text{P-C}) = 10.4$ Hz; PCCH), 136.68 (d, $^3J(\text{P-C}) = 5.8$ Hz; PCCHCH), 134.51 (s, SiC), 132.05 (d, $^2J(\text{P-C}) = 17.4$ Hz; PCCH), 20.11 (d, $^1J(\text{P-C}) = 12.4$ Hz; PCH_2), 10.06 (d, $^2J(\text{P-C}) = 14.1$ Hz; CH_3) ppm; ^{31}P NMR (C_6D_6 , 121.5 MHz): $\delta = -16.17$ ppm; ^{29}Si NMR (C_6D_6 , 99.4 MHz): $\delta = -14.9$ ppm. HR-MS (FAB⁺): $[\text{M}]^+$ (41.9%) 688.3041 (calcd. 688.3102), $[\text{M-Et}]^+$ (39.6%) 659.2729 (calcd. 659.2711), $[\text{M-PEt}_2]^+$ (11.9%) 599.2458 (calcd. 599.2582). (c) **Sn(p-C₆H₄Br)₄**: 1,4-Dibromobenzene (5.89 g, 24.97 mmol) was dissolved in 60 mL of ether and cooled to -15°C . Then 15.6 mL of a 1.6 M solution of $^n\text{BuLi}$ (24.97 mmol) in hexane was added dropwise. After having been stirred for 15 min the reaction mixture was cooled to -78°C , and 0.73 mL (6.25 mmol) of SnCl_4 was added dropwise. After the mixture was stirred for 12 h at ambient temperature, 20 mL of 1 M HCl was added, and the product was extracted with ether. The organic phase was washed with H_2O and dried with MgSO_4 . $\text{Sn}(p\text{-C}_6\text{H}_4\text{Br})_4$ was obtained after filtration, removal of the solvent in vacuo, and recrystallization with CHCl_3 as a colorless crystalline powder in 89.0% yield (4.12 g, 5.56 mmol), mp 214°C . ^1H NMR (CDCl_3): $\delta = 7.56$ (d, $^3J(\text{H-H}) = 8.1$ Hz, $^4J(^{119}\text{Sn-H}) = 12.1/7.6$ Hz, 8H; SnCCHCH), 7.39 (d, $^3J(\text{H-H}) = 8.1$ Hz, $^3J(^{119}\text{Sn-H}) = 47.6/45.7$ Hz, 8H; SnCCH), ^{13}C NMR (CDCl_3): $\delta = 138.29$ ($^2J(^{119}\text{Sn-C}) = 42.1/40.3$ Hz; SnCCH), 135.01 ($^1J(^{119}\text{Sn-C}) = 541.8/517.8$; SnC), 132.09 ($^3J(^{119}\text{Sn-C}) = 54.8/53.3$ Hz; BrCCH), 124.76 ($^4J(^{119}\text{Sn-C}) = 14.4$ Hz; BrC); ^{119}Sn NMR (CDCl_3 , 186.5 MHz): $\delta = -118.58$ ppm. HR-MS (FAB⁺): $[\text{M}]^+$ (55.9%) 739.6893 (calcd. 739.7007), $[\text{M-Br}]^+$ (29.8%) 660.7740 (calcd. 660.7824).
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