Table I. ^1H NMR (400 MHz, C_6D_6) and ^2H NMR (61.4 MHz, CCl_4)

		rel signal intensity			
		starting **1**-d_i		recovered **1**-d_i[b]	
H or D	δ ppm[a] (C_6D_6)	^1H NMR	^2H NMR	^1H NMR	^2H NMR
endo-6,7	1.65	1.947	0.123	1.890	0.163
endo-4 exo-6	2.05 2.10	1.345	1.038	1.314	1.019
exo-7	2.20	0.348	1.000	0.419	1.000
exo-4	2.45	0.998	0.076	0.967	0.074
5	2.72	1.000	0.009	1.000	0.012
1	3.15	0.984	0.019	0.979	0.016
2,3	5.70 5.75	1.897	0.047	1.914	0.047

[a] The signals for **1** were assigned by COSY 2D NMR and double resonance experiments. [b] From the thermolysis at 312 °C.

Table II. ^1H NMR (400 MHz, C_6D_6) and ^2H NMR (61.4 MHz, CCl_4) of **2**-d_i

		rel signal intensity	
H or D	δ ppm[a] (C_6D_6)	^1H NMR	^2H NMR
endo-5,6	0.94	1.222	1.000
anti-7	1.03	1.105	0.011
syn-7	1.29	1.000	0.016
exo-5,6	1.55	1.365	0.828
1,4	2.80	1.963	0.044
2,3	5.90	1.929	0.039

[a] For the ^1H NMR assignments in **2** see ref 9.

We have studied the stereochemical course of the [1,3] shift in the parent bicyclo[3.2.0]hept-2-ene only labeled by deuterium. Its experimental realization turned out to be difficult since at about 300 °C—the temperature required for the isomerization of **1**—norbornene (**2**) undergoes a retro-Diels–Alder reaction to give 1,3-cyclopentadiene (**3**) and ethene (**4**). Thus the maximum concentration of **2** to be expected is only about 1%.[3]

Catalytic reduction of bicyclo[3.2.0]hepta-2,6-diene (**5**)[4] with 1 mol equiv of deuterium (10% Pt/C, ether, room temperature) led to a mixture of deuteriated bicyclo[3.2.0]heptene **1**-d_i, bicyclo[3.2.0]heptane, and unconverted **5** in a (63:15:22) ratio as analyzed by GC.[5] From the ^1H and ^2H NMR spectrum of **1**-d_i isolated by preparative GC (Table I) the exo/endo selectivity in the deuteriation of the cyclobutene double bond is determined to be 96:4 and 94:6, respectively.[6a]

Thermolysis of **1**-d_i at 312 °C (240 min, gas phase, with cyclohexane as internal standard) produced a mixture of isomers: **1**-d_i (34%), norbornene **2**-d_i (1.3%), and five unidentified compounds (11%);[7] the only other products were cyclopentadiene (**3**) and deuteriated ethene (**4**-d_i). The deuterium distribution in **1**-d_i and **2**-d_i separated by GC[5] was again determined by ^1H and ^2H NMR spectroscopy (Tables I and II). The only slightly changed exo/endo ratio of deuterium at C-6,7 in recovered **1**-d_i (^1H NMR, 91:9, ^2H NMR, 93:7) shows that epimerization at C-6 and/or C-7 does not compete with the 1,3 shift to a significant extent. The stereochemical course of the 1,3 shift can now be calculated from the endo/exo ratio of deuterium at C-5,6 in the norbornene product **2**-d_i (Table II: ^1H NMR, 1.22; ^2H NMR, 1.21). Accordingly, the isomerization of **1** to **2** occurs with 89% inversion. An independent evidence for the predominant inversion process results from the *E*:*Z* ratio of the 1,2-dideuterioethene product which was analyzed by its characteristic IR bands at 987 and 843 cm^{-1} [8] to contain (82 ± 4)% of the *E* isomer.[6b]

The [1,3] rearrangement in the parent system shows a stereochemical course comparable with the classical example of *exo*-7-deuterio-*endo*-bicyclo[3.2.0]hept-2-en-6-yl acetate already mentioned.[2a] Obviously the acetoxy group at C-6 has only a minor effect on the stereochemistry of the [1,3] shift. The substantial component of retention (11%) observed here indicates that orbital symmetry cannot be the only factor which controls the course of reaction. As a reasonable explanation we suggest that a nonconcerted diradical pathway competes with the concerted process.[10,11] Similar results for the isomerization of **1** to **2** have been obtained independently by Baldwin and Belfield.[12]

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support and Professor J. E. Baldwin for sharing results in advance of publication.

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(5) GC analyses were performed on a 40-m silicon oil OV 101 glass capillary column at 25 °C. The products of catalytic reduction and thermolysis were separated on a 4-m squalane column at 78 °C.

(6) (a) The exo/endo selectivity in the catalytic deuteriation of norbornadiene proved to be 94:6. Thermolysis of the deuteriated norbornene product at 312 °C gave (*Z*)-1,2-dideuterioethene (≥97%). (b) The *E*:*Z* ratio in **4**-d_2—the product from the thermolysis of **1**-d_i—does not deviate from the inversion/retention ratio found in **2**-d_2 significantly within the limits of error of the IR analysis. Thus only a minor component of **4**-d_2 might stem directly from **1**-d_2.

(7) The unidentified compounds could be secondary products from the cleavage of cyclobutane bonds C-1–C-5 and C-6–C-7 in **1**, see ref 3.

(8) Calibration data reported in the dissertation by Cannarsa (Cannarsa, M. J. *The Synthesis and Thermolysis of Stereospecifically Labeled 1,2,3,4-Cyclobutanes-*d_4; Cornell University, 1984) were used for the IR analysis of the *E*:*Z* ratio of 1,2-dideuterioethene.

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(10) As an alternative interpretation a stereoselective diradical process cannot be excluded as has also been suggested for the [1,3] shift in substituted bicyclo[2.1.1]hex-2-ene systems. Newman-Evans, R. H.; Carpenter, B. K. *J. Am. Chem. Soc.* **1984**, *106*, 7994–7995. Carpenter, B. K. *J. Am. Chem. Soc.* **1985**, *107*, 5730–5732.

(11) According to a thermochemical estimate the enthalpy of formation of the transition state ($\Delta H_f°(TS) = \Delta H_f°(\mathbf{1}) + \Delta H^*(\mathbf{1} \rightarrow \mathbf{3} + \mathbf{4}) = 28.6 + 49.2^3 = 77.8$ kcal/mol) is higher by 1.3 kcal/mol than that of the corresponding diradical calculated by molecular mechanics; thus the energy of concert for reaction **1** → **2** appears to be negligible: Doering, W. v. E.; Roth, W. R.; Breuckmann, R.; Figge, L.; Lennartz, H.-W.; Fessner, W.-D.; Prinzbach, H. *Chem. Ber.*, in press. $\Delta H_f°(\mathbf{1})$ was determined from the heat of hydrogenation of **1** ($\Delta H_H = -27.9$ kcal/mol) and a MM2 calculation of $\Delta H_f°$ (bicyclo[3.2.0]heptane). Roth, W. R.; Lennartz, H.-W., unpublished results.

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Synthesis by Spontaneous Self-Assembly of Metal Atom Clusters of Zirconium, Niobium, and Tantalum

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Systematic, designed preparative methods for obtaining metal atom cluster species are obviously desirable but rarely devised. However, spontaneous self-assembly occurs and can be exploited. We report here three such reactions, each of which leads to a product that is of unusual interest in its own right and also possesses potential for further synthetic development.

There are several previous reports of trinuclear, triangular cluster species of niobium comprising both the bicapped[1] $[Nb_3(\mu_3\text{-}O)_2]$ and $Nb_3(\mu_3\text{-}X)(\mu\text{-}X)_3$ type cores. Most recently we described the compound $Nb_3(\mu_3\text{-}Cl)(\mu\text{-}Cl)_3Cl_3(PMe_2Ph)_6$[2] which has an eight-electron core configuration and a mean Nb–Nb

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(1) Cotton, F. A.; Diebold, M. P.; Llusar, R.; Roth, W. J. *J. Chem. Soc., Chem. Commun.* **1986**, 1276.

(2) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 2833.

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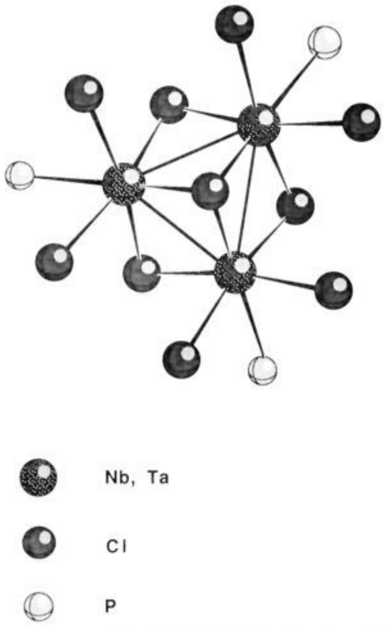

Figure 1. The structure of the $[M_3Cl_{10}(PEt_3)_3]^-$ anions (M = Nb, Ta). The idealized symmetry is C_{3v}. Ethyl groups are omitted.

Table I. Important Averaged Interatomic Dimensions in $[M_3Cl_{10}(PEt_3)_3]^-$ (M = Nb and Ta) and $Nb_3Cl_7(PMe_2Ph)_6$

	$[M_3Cl_{10}(PEt_3)_3]^-$		
	Nb	Ta	$Nb_3Cl_7(PMe_2Ph)_6$
M–M	2.976 (6)	2.932 (3)	2.832 (4)
$M-Cl_{cap}$	2.504 (1)	2.498 (7)	2.470 (5)
$M-Cl_{bridge}$	2.443 (4)	2.431 (3)	2.476 (3),[a] 2.531 (4)[b]
$M-Cl_{terminal}$	2.424 (4)	2.413 (6)	2.485 (6)
M–P	2.667 (3)	2.649 (2)	2.696 (2),[b] 2.731 (8)[c]
$M-Cl_{cap}-M$	72.9 (2)	71.9 (1)	70.0 (1)
$M-Cl_{bridge}-M$	75.05 (7)	74.2 (2)	68.9 (2)

[a] Cl trans to $Cl_{terminal}$. [b] Cl_{bridge} and P atoms trans to each other. [c] P trans to Cl_{cap}.

distance of 2.831 (3) Å. *No tantalum analogue to any of these Nb_3 species has been reported.*

We have now prepared both $[Nb_3(\mu_3\text{-}Cl)(\mu\text{-}Cl)_3Cl_6(PEt_3)_3]^-$ (**1**) and its tantalum analogue **2** as their $[PEt_3H]^+$ salts and characterized them by X-ray crystallography.[3,4] The niobium anion is shown in Figure 2; the Ta anion is very similar (cf. Table I). The niobium compound is obtained by reducing $NbCl_4(THF)_2$ + $2PEt_3$ in toluene with 1 equiv of Na/Hg and diffusing hexane into the solution to cause crystallization of the red product. The green tantalum analogue is made in a similar way from $TaCl_5$ + $2PEt_3$ and 2Na/Hg. In each case the yield is 30–35%. The compounds are only slightly air-sensitive, which is surprising when the properties of most Nb^{III} and Ta^{III} compounds are considered.

The average values of important distances and angles in the trinuclear anions of **1** and **2** are listed in Table I along with those of the $Nb_3Cl_7(PMe_2Ph)_6$ molecule. It is noteworthy that all distances in **2** are shorter than those in **1**, especially the M–M distance. Of even more interest is the fact that in the anion of **1**, which has a six-electron cluster population, the Nb–Nb distance is ca. 0.15 Å longer than that in the eight-electron species $Nb_3Cl_7(PMe_2Ph)_6$. Previous theoretical studies[5] of $M_3(\mu_3\text{-}X)$-$(\mu\text{-}X)_3$-type clusters have indicated that the three lowest lying cluster-based orbitals include strongly bonding *a* and *e* types, followed by an approximately nonbonding *a* orbital. Apparently in the Nb_3Cl_4-type clusters the second *a* orbital is appreciably bonding in character, since addition of two electrons to the a^2e^4 configuration causes such a large contraction in the M–M distances.

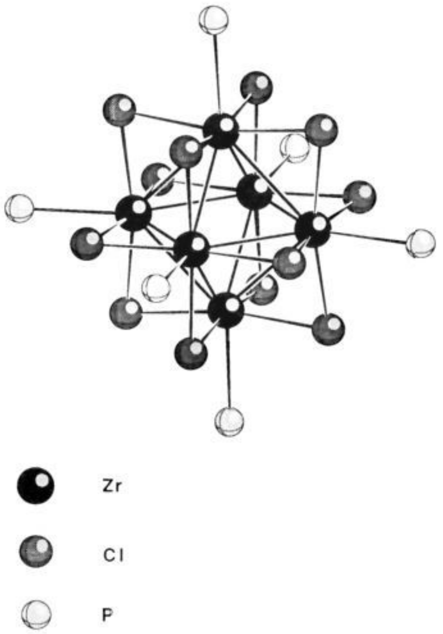

Figure 2. The structure of the $Zr_6Cl_{12}(PMe_2Ph)_6$ molecule, which has idealized O_h symmetry. Methyl and phenyl groups are omitted.

As part of our general interest in edge-sharing bioctahedral compounds of the general type $M_2X_4L_4(\mu\text{-}Y)_2$ (where Y may be equal to X) we have explored the chemistry of $Zr_2X_6(PR_3)_4$ compounds[6] as well as their Hf analogues. In the course of these studies we previously noted that when solutions of these green compounds are heated they turn red irreversibly. We have now been able to obtain a crystalline product from one of these solutions (employing $Zr_2Cl_6(PMe_2Ph)_4$) and have determined its structure, Figure 2, by X-ray crystallography.[7] We have no evidence that this is actually present in solution, since NMR spectra (^{31}P) are complex and not yet understood.

The spontaneity with which this $Zr_6Cl_{12}(PMe_2Ph)_6$ molecule (**3**) self-assembles under very mild conditions is remarkable. Beyond that the molecule of **3** is of great interest when compared with a series of compounds containing $(Zr_6X_{12})^{n+}$ units that Corbett and co-workers have studied for many years.[8] Although they were originally formulated as substances with empty Zr_6X_{12} cages linked together by additional bridging X atoms, occupying the positions occupied by the phosphorus atoms of our compound, more recent work has shown that in every case that has been more carefully studied, an atom occupies the Zr_6 octahedral cage. Representative examples are $Zr_6I_{12}C$, $Zr_6Cl_{15}N$, $KZr_6Cl_{13}Be$, and $K_2Zr_6Cl_{15}B$. It appears that in early work the trapped atoms (N, C) entered adventitiously, but it is now known that they can be introduced deliberately. In all cases, these materials are prepared by thermal reactions at high temperatures (700–850 °C). Corbett's recent characterizations (or recharacterizations) of his

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(3) Compound **1**: monoclinic cell ($P2_1/n$) with a = 12.615 (1) Å, b = 18.731 (3) Å, c = 23.662 (4) Å, β = 98.59 (1)°, V = 5528 (2) Å^3, Z = 4, and d_{calcd} = 1.468 g/cm^3 for f_w = 1222.01. Refinement of 399 parameters using 5505 observables with $F^2 > 3\sigma(F^2)$ gave residuals R and R_w equal to 0.047 and 0.067, respectively.

(4) Compound **2**: monoclinic cell ($P2_1/n$) with a = 11.864 (3) Å, b = 20.664 (2) Å, c = 18.779 (2) Å , β = 97.61 (2)°, V = 4563 (2) Å^3, Z = 4, and d_{calcd} = 1.993 g/cm^3 for f_w = 1371.02. Refinement of 325 parameters using 4047 observables with $F^2 > 3\sigma(F^2)$ gave residuals R and R_w equal to 0.039 and 0.048, respectively.

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(6) Cotton, F. A.; Diebold, M. P.; Kibala, P. A. *Inorg. Chem.*, in press.

(7) The compound crystallized in an orthorhombic space group $P2_12_12_1$ with a = 20.896 (3) Å, b = 22.545 (3) Å, c = 14.735 (1) Å, V = 6941 (2) Å^3, Z = 4, and d_{calcd} = 1.724 g/cm^3 for f_w = 1801.7. Refinement of 302 parameters using 2496 reflections having $F^2 > 3\sigma(F_2)$ gave R = 0.0579 and R_w = 0.0768. The data reported are for the enantiomer that gave lower R and R_w values.

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compounds raise the question of whether the Zr_6X_{12} unit can (or ever does) exist empty.

We do not think it likely that there is any atom occupying the Zr_6 cage in $Zr_6Cl_{12}(PMe_2Ph)_6$. The presence of C, N, or any heavier atom could scarcely escape our notice. The presence of Be or B seems unplausible for chemical reasons alone. Only H (or H_2) might be chemically possible and crystallographically acceptable.

The $Zr_6Cl_{12}(PMe_2Ph)_6$ molecule has a mean Zr–Zr distance of 3.223 (3) Å, and there are 12 electrons for Zr_6 cluster bonding. In the occupied cages mentioned above, there are generally 14 electrons and Zr–Zr distances of ca. 3.21 Å. The addition of two electrons would increase the Zr–Zr bond order only from 0.50 to 0.58 which does not seem inconsistent with the slight change in Zr–Zr distance.

Acknowledgment. We thank the National Science Foundation and the Robert A. Welch Foundation for support.

Supplementary Material Available: Tables of atomic positional and isotropic equivalent thermal parameters, anisotropic thermal parameters, and bond distances and bond angles for **1**, **2**, and **3** (28 pages). Ordering information is given on any current masthead page.

The ab Initio Energy Difference Favoring the Nonclassical over the Classical Structure of the Bicyclo[2.1.1]hexyl Cation. Comparison of Calculated (IGLO) and Experimental ^{13}C Chemical Shifts

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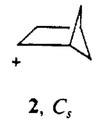
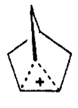
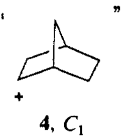
Despite the inherent investigational advantage that both nonclassical **1** and classical **2** forms possess C_s symmetry, the 2-bicyclo[2.1.1]hexyl cation[1] has received only a fraction of the attention[1-3] afforded its infamous homolog, the 2-norbornyl cation, **3**[4] (**4** is a hypothetical species).[5] Nevertheless, data pertinent to the structure (**1** vs **2**) of the bicyclohexyl cation are rather extensive, but there has been disagreement regarding the intepretation.[1-3,6-12] The problem is not a simple one. As all three methylene groups are equivalent on the NMR time scale at −110°, and no CMR line broadening is observed, the energy difference between **1** and **2** must be 3 kcal/mol or less.[6,7,9] The isotopic perturbation method clearly indicates that the stable ion has the bridged structure.[9] Kirmse's impressive recent double labeling experiments indicated that **1** should be about 3 kcal/mol more


1, C_s


2, C_s


3, C_s


4, C_1

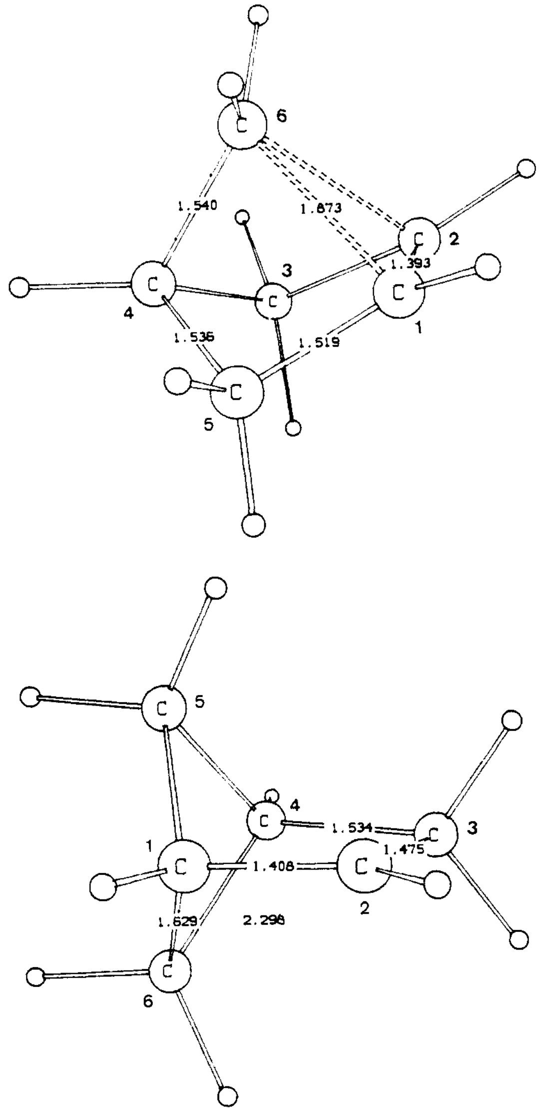


Figure 1. MP2(FULL)/6-31G* geometries of the bridged **1** (top) and classical **2** (botton) 2-bicyclo[2.1.1]hexyl cations. For bicyclo[2.1.1]hexane **5** at the same level, $r(C_1C_2)$ = 1.533, $r(C_1C_6)$ = 1.546, and $r(C_2C_3)$ = 1.557 Å.

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(1) First investigated by the following: (a) Meinwald, J.; Gassman, P. G.; Hurst, J. J *J. Am. Chem. Soc.* **1962**, *84*, 3722. (b) Meinwald, J.; Gassman, P. G. *Ibid.* **1963**, *85*, 27. (c) Meinwald, J.; Crandell, J. K. *Ibid.* **1966**, *88*, 1292. (d) Meinwald, J.; Shelton, J. C.; Buchanan, G. L.; Courtin, A. *J. Org. Chem.* **1968**, *33*, 99. Also, see: (e) Brown, H. C.; Ravinchandran, M.; Rao, C. G. *Ibid.* **1977**, *94*, 2360. (f) Foote, C. S. *Ibid.* **1964**, *86*, 1853. (g) Schleyer, P. v. R. *Ibid.* **1964**, *86*, 1857. (g) Müller, P.; Mareda, J. *Helv. Chim. Acta* **1985**, *68*, 119. Cf. Müller, P.; Mareda, J. *Ibid.* **1987**, *70*, 1017.

(2) Recent reviews: (a) Vogel, P. *Carbocation Chemistry*; Elsevier: 1985; pp 151, 281, 361. (b) Olah, G. A.; Surya Prakash, G. K.; Sommer, J. *Superacids*; Wiley: 1985; p 142. (c) Ahlberg, P.; Jonsäll, G.; Engdahl, C. *Adv. Phys. Org. Chem.* **1983**, *19*, 223.

(3) Leading reference: Kirmse, W.; Zellmer, V.; Goer, B. *J. Am. Chem. Soc.* **1986**, *108*, 4912. Also, see: Kirmse, W.; Streu, J. *J. Org. Chem.* **1987**, *52*, 515.

(4) Brown, H. C. (with comments by Schleyer, P. v. R.) *The Nonclassical Ion Problem*; Plenum: 1977.

(5) The only 2-norbornyl cation minimum is the bridged structure **3** with C_s symmetry: (a) Raghavachari, K.; Haddon, R. C.; Schleyer, P. v. R.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1983**, *105*, 5915. (b) Yoshimine, M.; McLean, A. D.; Liu, B.; DeFrees, D. J.; Binkley, J. S. *Ibid.* **1983**, *105*, 6185.

(6) Seybold, G.; Vogel, P.; Saunders, M.; Wiberg, K. B. *J. Am. Chem. Soc.* **1973**, *95*, 2045.

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