sample was referenced. In order to eliminate artifacts generated by the presence of *cis*-d_2-cyclopropane in kinetic samples, the VCD spectrum of the (−)-*R*,*R* kinetic sample was referenced against racemic trans containing the same amount of cis isomer present in a kinetic sample. VCD intensities of the resulting base-line-corrected spectra were measured in volts relative to the racemic base line for 90 data points between 2310 and 2290 cm^{-1}. The ratios of all 90 data points were averaged to obtain a measure of the ratio $|\Delta A/\Delta A_{\text{ref}}|$ for each kinetic sample (Table I). Four separate determinations of $|\Delta A/\Delta A_{\text{ref}}|$ were performed on successive days for each sample. A nonlinear least-squares treatment of the data for the chiral kinetic samples gave rate constant $k_\alpha = (12.3 \pm 0.65) \times 10^{-5}$ s^{-1} (SD, three kinetic points).

With VCD spectroscopy, it was possible to use samples between 2 and 3 orders of magnitude smaller than those employed by Berson and Pedersen[7] using optical polarimetry, thus greatly alleviating difficulties posed by synthetic and gas chromatographic problems of scale, and of expense. The promise of VCD spectroscopy for kinetic studies[13] seems very bright indeed.

The present determinations of k_i and k_α are each about twice as large as the values reported earlier,[7] which could easily be associated with small differences in temperature, pressure, or bath-gas effects; yet the ratio of rate constants now found, $k_i/k_\alpha = 1.09 \pm 0.05$, is in fine agreement with the report of Berson and Pedersen.[7] The final resolution of the problem posed by the apparently dichotomous stereomutation propensities of deuterium-labeled cyclopropanes and other substituted cyclopropanes must await either new information relevant to the deuterium kinetic isotope effects that may be in play, or experiments with some new set of labeled isomers, providing as many experimentally measurable rate parameters as there are distinct rate constants for one-center and two-center epimerizations to be derived. One may even now, though, be more assured that the problem is not an illusion predicated on an inaccurate experimental value for k_i/k_α.

Acknowledgment. We thank Professor David K. Lewis and his associates at Colgate University and Dr. David A. Glenar of the NASA Goddard Space Flight Center for many helpful exchanges of information and perspectives and the National Science Foundation for support of this work through CHE-86-02854 and CHE-87-21656.

Unprecedented, Bridged Dihydrogen Complex of a Cofacial Metallodiporphyrin and Its Relevance to the Bimolecular Reductive Elimination of Hydrogen

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Recently, we characterized the first metalloporphyrin dihydrogen complex, Os(OEP)(H_2), and proposed that a similar ruthenium porphyrin dihydrogen complex, Ru(OEP)(H_2), is involved as an intermediate in the catalytic H/D isotopic exchange between water and hydrogen.[2,3] We now report that treatment of a metal–metal-bonded cofacial ruthenium porphyrin dimer with a sterically bulky ligand in the presence of hydrogen gas has yielded the first known complex containing a dihydrogen ligand bound between two metals. Such a bridged dihydrogen complex is proposed as an intermediate in the bimolecular elimination of dihydrogen from two metalloporphyrin hydrides.

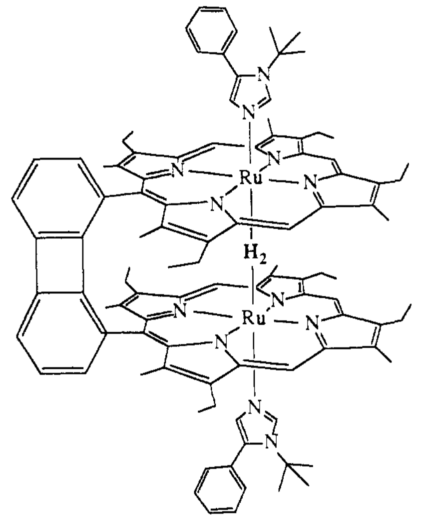

Figure 1.

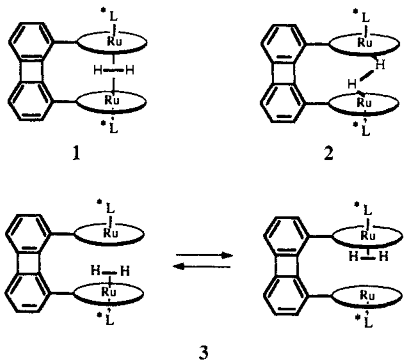

Figure 2.

Addition of 2 equiv of 1-*tert*-butyl-5-phenylimidazole, *L, to a hydrogen-saturated benzene solution of the cofacial metalloporphyrin dimer Ru_2(DPB)[4] resulted in the immediate formation of Ru_2(DPB)(*L)$_2$(H_2),[5] which displayed a broad singlet at $\delta = -38.6$ ppm in the ^{1}H NMR spectrum,[6] indicating the presence of a metal-bound hydride or dihydrogen ligand.[7] When the same reaction was performed with hydrogen deuteride (instead of hydrogen), the broad singlet was replaced by a 1:1:1 triplet at $\delta = -38.4$ ppm ($^1J_{HD} = 15 \pm 1$ Hz) while the rest of the ^{1}H NMR spectrum remained unchanged. Additionally, the minimum relaxation time of the metal-bound protons was 132 ± 6 ms as determined by variable-temperature ^{1}H NMR measurements (400 MHz, 20 °C, toluene-d_8).[9,10] These values for $^1J_{HD}$ and T_1(min)

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(2) Abbreviations: OEP = octaethylporphyrinato dianion; DPB = diporphyrinatobiphenylene tetraanion; THF = tetrahydrofuran; PPh_3 = triphenylphosphine; $FeCp_2$ = ferrocene.

(3) Collman, J. P.; Wagenknecht, P. S.; Hembre, R. T.; Lewis, N. S. *J. Am. Chem. Soc.* **1990**, *112*, 1294–1295.

(4) Collman, J. P.; Kim, K.; Leidner, C. R. *Inorg. Chem.* **1987**, *26*, 1152–1157.

(5) Under an argon atmosphere, a solution of Ru_2DPB in d_6-benzene (0.5 mL of a 1.38 mM stock solution) was bubbled for 5 min with hydrogen. Two equivalents of 1-*tert*-butyl-5-phenylimidazole (58 μL of a 26.5 mM stock solution in d_6-benzene) was added, and hydrogen bubbling was continued for 2 min.

(6) ^{1}H NMR (C_6D_6, ppm): porphyrinic resonances, H_{meso} 8.81 (s, 2 H), 8.72 (s, 4 H); biphenylene 7.15 (2 H, obscured by residual solvent peak), 7.06 (d, 2 H), 6.85 (t, 2 H): CH_2CH_3 4.38 (m, 8 H), 3.91 (m, 8 H); CH_3 3.50 (s, 12 H), 3.25 (s, 12 H); CH_2CH_3 1.81 (t, 12 H), 1.61 (t, 12 H); imidazole resonances, *p*-phenyl 6.21 (t, 2 H); *m*-phenyl 5.99 (t, 4 H); *o*-phenyl 4.38 (d, 4 H); $H_{imidazole}$ −0.34 (s, 2 H), −0.40 (s, 2 H); *tert*-butyl −0.86 (s, 18 H). Ru–H_2 −38.6 (br s, 2 H). Ru–HD −38.4 (t, $^1J_{HD} = 15 \pm 1$ Hz).

(7) The hydride and dihydrogen ligand resonances of metalloporphyrins are shifted to very high field in the ^{1}H NMR spectra by the porphyrin ring current effect.[3,8]

(8) Collman, J. P.; Brothers, P. J.; McElwee-White, L.; Rose, E. *J. Am. Chem. Soc.* **1985**, *107*, 6110–6111.

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fall within the limits proposed for classification as a dihydrogen complex[11-16] and very closely match the corresponding values of the previously reported metalloporphyrin dihydrogen complex, $Os(OEP)(H_2)$.[3] These spectroscopic properties indicate that $Ru_2(DPB)(*L)_2(H_2)$ contains a metal-bound dihydrogen. The location of this dihydrogen ligand has been elucidated from additional ^1H NMR data.

The ^1H NMR spectrum displayed only one set of porphyrinic resonances for $Ru_2(DPB)(*L)_2(H_2)$, indicating that only a single type of porphyrin is present (i.e., the two porphyrins of the DPB ligand are equivalent on the time scale of the NMR experiment).[6] Even at −80 °C, though the porphyrin resonances are broadened and the hydride resonance shifts 0.5 ppm upfield, the resonances of the two porphyrins remain equivalent. This C_2 symmetry precludes complexes containing a single molecule of dihydrogen bound to a single metal. Additionally, integration of the ^1H NMR signals showed that each $Ru_2(DPB)(*L)_2(H_2)$ contained only one molecule of dihydrogen[17] and two equivalent, axial ligands.[6] Consequently, the axial ligands must be coordinated to the outside faces of the diporphyrin with the dihydrogen symmetrically bound between the two metals (Figure 1). Though bimetallic complexes containing dihydrogen ligands are known,[18] to our knowledge this is the first complex that binds dihydrogen between the two metals.

The spectroscopic data suggest three possible modes of binding (Figure 2). Structures **1** and **2** are static and represent true bridging structures. Because the metal–metal distance for a $M_2(DPB)$ system with the metals bound in the porphyrin plane is 3.8 Å,[19] structure **1** should require a metal–H_2 distance of 1.9 Å. This distance is 0.2 Å greater than the longest known, stable metal–H_2 distance,[20] but similar to the distance determined by ab initio calculations for the Cr–H_2 bond in the thermally unstable $Cr(CO)_5(H_2)$ complex.[21] Structure **2** is also a candidate because tilting the dihydrogen ligand may enhance the overlap between the Ru d_{xz} and d_{yz} and the H_2 σ^* orbitals. An equally likely formulation, structure **3**, is dynamic and would not represent a true bridging structure. However, we are unable to observed a splitting of the C_2 symmetry at −80 °C on the NMR time scale.

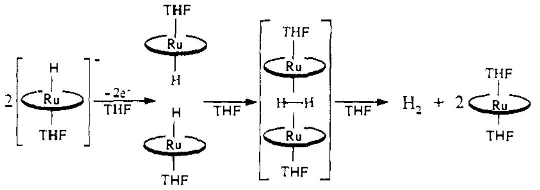

Figure 3.

This structural ambiguity cannot be fully resolved without a neutron diffraction structure.

This binding of dihydrogen is dependent on the nature of the axial ligand. The metal–metal-bonded dimer, Ru_2DPB, did not react with hydrogen in the absence of added imidazole, nor does the previously reported $Ru_2DPB(PPh_3)_2$ (with the PPh_3 ligands on the outside faces of the metallodiporphyrin)[4] bind dihydrogen.

Although $Ru_2(DPB)(*L)_2(H_2)$ is stable in solution for more than a day at room temperature under 1 atm of hydrogen, the dihydrogen ligand dissociated when the solution was heated. Furthermore, dihydrogen is replaced in minutes by dinitrogen to yield a bridged dinitrogen complex, and by pyridine to yield the complex with two pyridine ligands bound in the cavity of the diporphyrin.[22] Replacement by deuterium gas occurs without scrambling to give $Ru_2(DPB)(*L)_2(D_2)$; formation of $Ru_2(DPB)(*L)_2(HD)$[6] was not observed.

The spectroscopic properties of $Ru_2(DPB)(*L)_2(H_2)$ show no obvious ruthenium(III) hydride character and suggest that a dihydrogen molecule bridging two ruthenium(II) centers is more stable than two opposing ruthenium(III) hydrides. This proposal may be further tested by generating monomeric ruthenium(III) hydrides and studying their reactivity. Cyclic voltammetry shows that the previously reported ruthenium(II) hydride, K[Ru(OEP)(H)],[8] **Ru(II)H⁻**, undergoes an oxidation at −1.15 V (vs $FeCp_2^{+/0}$), which is irreversible (the ratio of the cathodic current to the anodic current decreased with decreasing scan rates).[23] Attempts to prepare chemically the ruthenium(III) hydride, **Ru(III)H**, through the oxidation of a 2 mM solution of **Ru(II)H⁻** by VBr_3 in dry THF, failed. Oxidation is followed by a chemical step producing H_2 and the ruthenium(II) species $Ru(OEP)(THF)_2$, as identified and quantified by gas chromatography and ^1H NMR, respectively. This reaction was further studied by double potential step chronoamperometry (DPSC). Cathodic to anodic current ratios[24] obtained from DPSC for a series of **Ru(II)H⁻** concentrations were compared to theoretical first-order[24] and second-order[25] kinetic models. The results of this comparison clearly indicate that subsequent to oxidation the ruthenium hydride undergoes a second-order reaction (with respect to [Ru]) with a rate constant of 88 ± 14 M^{-1} s^{-1}. Similar reactivity is observed when *L is coordinated trans to the hydride in the complex K[Ru(OEP)(*L)(H)].

On the basis of these results, we propose that **Ru(III)H** is being produced by oxidation of the **Ru(II)H⁻**, but is unstable with respect to bimolecular elimination of hydrogen. The elimination likely involves a transition state in which two **Ru(III)H** molecules approach each other hydride to hydride. Subsequent reductive elimination of hydrogen results in a dihydrogen-bridged species similar to the proposed structure of $Ru_2(DPB)(*L)_2(H_2)$. The flexibility of the dihydrogen-bridged, monomeric porphyrins presumably allows this structure to dissociate rapidly to give free hydrogen and $Ru(OEP)(THF)_2$ (Figure 3). The reverse of this reaction scheme represents a key process in the possible bimetallic, homolytic activation of dihydrogen.[26] Further studies are in

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(9) T_1 values were measured by the standard method of inversion recovery (400-MHz NMR).

(10) (a) This relatively high temperature for T_1(min) is probably due to the large molecular volume of the cofacial porphyrin. The minimum T_1 occurs when $\tau_c\omega$ = 0.63, where τ_c is the molecular correlation time and ω is the resonant frequency. Because $\tau_c \propto V/T$, where V is the molecular volume, and T is temperature, T_1(min) occurs at higher temperatures for larger H_2 complexes. Bovey, F. A. et al. *Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; Academic Press, Inc.: San Diego, 1988. (b) References 15a and 15c, this paper.

(11) $^1J_{HD}$ values for cis dihydrides are typically <1 Hz,[12] an order of magnitude smaller than those typical of dihydrogen complexes.[13]

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(13) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120–128 and references therein.

(14) The upper limit for T_1 of a dihydrogen complex is suggested as ≃160 ms at 400 MHz.[15,16]

(15) (a) Crabtree, R. H.; Hamilton, D.; Lavin, M. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; pp 223–226. (b) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126–4133. (c) Bautista, M. T.; Kelly, A. E.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T.; Sella, A. *J. Am. Chem. Soc.* **1988**, *110*, 7031–7036. (d) Luo, X.; Crabtree, R. H. *Inorg. Chem.* **1990**, *29*, 2788–2791.

(16) The reliability of T_1 measurements in predicting whether polyhydride complexes contain molecular hydrogen ligands has recently been questioned for complexes where the number of metal-bound hydrogen atoms is greater than two. (a) Cotton, F. A.; Luck, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 5757–5761. (b) Cotton, F. A.; Luck, R. L.; Root, D. R.; Walton, R. A. *Inorg. Chem.* **1990**, *29*, 43–47.

(17) The ratio of Ru:H_2 = 2:1 was verified by displacing the dihydrogen ligand with pyridine and quantifying the H_2 by gas chromatography of the reaction vessel headspace.

(18) (a) Hampton, C.; Dekleva, T. W.; James, B. R.; Cullen, W. R. *Inorg. Chim. Acta* **1988**, *145*, 165–166. (b) Arliguie, T.; Chaudret, B.; Morris, R. H.; Sella, A. *Inorg. Chem.* **1988**, *27*, 598–599. (c) Hampton, C.; Cullen, W. R.; James, B. R. *J. Am. Chem. Soc.* **1988**, *110*, 6918–6919.

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(21) Pacchioni, G. *J. Am. Chem. Soc.* **1990**, *112*, 80–85.

(22) Collman, J. P.; Hutchison, J. E.; Wagenknecht, P. S., manuscript in preparation.

(23) All electrochemical experiments were performed in an argon, inert atmosphere box employing a silver wire reference electrode in a luggin capillary with a platinum disk working electrode and a platinum wire auxiliary electrode. Metalloporphyrin concentrations ranged from 2 to 8 mM in THF with 0.2 M tetrabutylammonium hexafluorophosphate as the backing electrolyte. $FeCp_2$ was added as a reference at the conclusion of each experiment.

(24) Schwarz, W. M.; Shain, I. *J. Phys. Chem.* **1965**, *69*, 30–40.

(25) Olmstead, M. L.; Nicholson, R. S. *Anal. Chem.* **1969**, *41*, 851–852.

progress to further elucidate this mechanism by varying the electronic and steric properties of the metalloporphyrin. We also plan to examine Ru_2(DPB) as a possible hydrogen electrode catalyst.

Acknowledgment. J.E.H. acknowledges support from the Franklin Veatch Memorial Fellowship fund, 1987–1989. P.S.W. acknowledges support as a National Science Foundation Graduate Research Fellow, 1986–1989. Support from the National Science Foundation, the National Institutes of Health, and the Gas Research Institute is acknowledged. Helpful discussions with Professor Jack Norton and Professor Royce Murray are gratefully acknowledged. Contribution No. 8152 from the Division of Chemistry and Chemical Engineering, California Institute of Technology.

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Stereoselective Synthesis of Olefins from Silylated Sulfonylhydrazones

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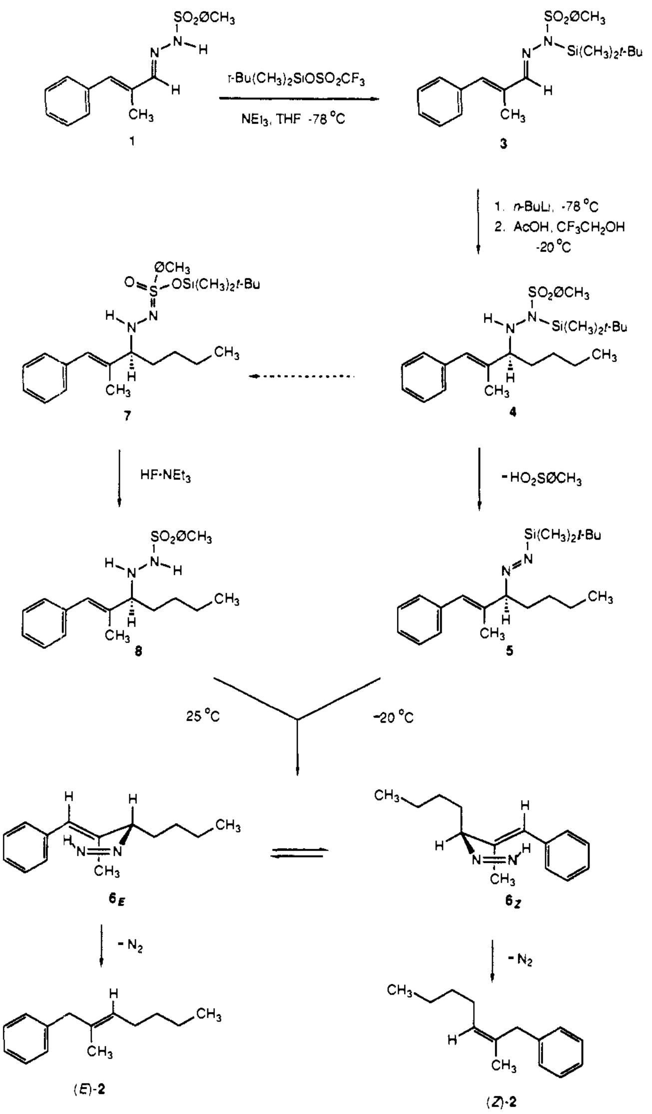
Aldehyde tosylhydrazones have previously been shown to react with alkyllithium or cuprate reagents to form anionic addition products. The reaction requires 2 equiv or more of the organometallic reagent to proceed to completion and is presumed to occur by the elimination of dinitrogen from an intermediate dianion.[1] We find that aldehyde tosylhydrazones can be transformed into stable *N-tert*-butyldimethylsilyl derivatives which undergo smooth 1,2-addition with equimolar quantities of organolithium reagents.[2] The resulting adducts can be induced to decompose along a different pathway than previously observed, by sigmatropic rearrangement of a proposed allylic diazene intermediate, to afford olefinic products.[3] The method and mechanistic details pertinent to the process are illustrated in the conversion of (*E*)-α-methylcinnamaldehyde tosylhydrazone (**1**)[4] to the *E*-trisubstituted olefin **2** (Scheme I).

Scheme I



Triethylamine (1.25 mmol) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (1.15 mmol) are added sequentially to a solution of tosylhydrazone **1** (1.0 mmol)[4] in anhydrous tetrahydrofuran (THF, 5 mL) at −78 °C. Methanol (1.25 mmol) is added after 30 min, and the cold reaction mixture is partitioned between hexanes and saturated aqueous sodium bicarbonate solution to afford, upon concentration of the organic layer, the *N-tert*-butyldimethylsilyl sulfonylhydrazone **3** in near quantitative yield. These derivatives vary in their stability toward silica gel and, in general, are used directly without purification. That silylation occurs on nitrogen and not a sulfonamide oxygen is ascertained by ^{15}N NMR spectroscopy (**3**: δ −42.2, −209.9 vs external HNO_3, $CDCl_3$, 0.03 M Cr(acac)$_3$).[5] The conversion of **3** to olefin **2** is accomplished in a single operation, as follows. A deoxygenated solution of crude **3** in THF (5 mL) is cooled to −78 °C and treated with *n*-butyllithium (1.15 mmol, 1.6 M in hexanes). Acetic acid (1.2 mmol) is added after 15 min followed by the cosolvent 2,2,2-trifluoroethanol (10 mL), and the mixture is brought to −20 °C and held at that temperature for 12 h. Extractive isolation and flash column chromatography provide the olefin **2** as a 12:1 mixture of *E* and *Z* isomers, respectively, in 88% yield from **1**.

The formation of **2** from **3** is believed to proceed by the sequence **3** → **4** → **5** → **6** → **2** (Scheme I), a conclusion drawn from the following observations. Intermediate **4** rearranges upon attempted isolation to form **7**, the product of N → O silyl migration. This rearrangement is not observed in the reaction medium described, but does occur if excess acetic acid is employed in the quenching step. Unlike **4**, **7** is stable under the conditions of olefin formation and can be purified by flash column chromatography. Inter-

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(1) (a) Vedejs, E.; Stolle, W. T. *Tetrahedron Lett.* **1977**, 135. (b) Bertz, S. H. *Tetrahedron Lett.* **1980**, *21*, 3151.

(2) Organolithium additions to cinnamaldehyde tosylhydrazone proceed in 1,4 fashion (ref 1a).

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(4) (*p*-Tolylsulfonyl)hydrazine (2.10 mmol) and (*E*)-α-methylcinnamaldehyde (2.00 mmol) were combined in tetrahydrofuran (10 mL) at 23 °C, the mixture was stirred at 23 °C for 1 h, and the solution was concentrated. Recrystallization of the solid residue (ether–petroleum ether–methanol, 20:5:1) afforded pure **1** (0.58 g, 93%, mp 124–126 °C dec).

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