are as typically found for many other bent metallocene complexes.[5] It is doubly bridged to an ordinary $Al(CH_3)_2$ group [bond distances Al–C10 = 1.953 (8) Å, Al–C11 = 1.958 (4) Å; bond angle C10,Al,C11 = 117.4 (4)°]. The very nature of the two bridging ligands in **8a** is quite remarkable. To our knowledge, the Al,Zr(μ-C≡CPh) unit in **8a** represents one of the very few examples exhibiting a μ-alkynyl linkage between a transition and main-group metal.[6] Its bonding situation is structurally and stereoelectronically related to what is found in M(CO)M complexes exhibiting a semibridging carbon monoxide ligand.[7] In **8a** the Zr–C12 separation is 2.340 (3) Å whereas the Al–C12 bond distance is 2.103 (5) Å. The bonding parameters of the C≡CR unit are 1.209 (4) Å (C12–C13), 1.438 (4) Å (C13–C14), and 179 (2)° (C12,C13,C14). The C12,C13,C14 vector is oriented coplanar with the central metallacyclic framework. The C≡C triple bond is slightly leaning over toward the aluminum atom [bond angles around C12 = 110 (1) (C13,C12,Al), 162.8 (4) (C13,C12,Zr), 86.4 (4)° (Al,C12,Zr)].

The extraordinary geometric arrangement of the other bridging ligand between Al and Zr represents the truly outstanding structural feature of **8a**. The MeCCPh moiety is bonded to zirconium by means of carbon atom C1 [bond distances C1–Zr = 2.163 (3) Å, C1–C2 = 1.497 (6) Å, C1–C3 = 1.324 (4) Å; angles C2,C1,C3 = 129.2 (4)°, Zr,C1,C3 = 86.6 (6)°] and to zirconium *and* aluminum by means of C3. This additional strong carbon to zirconium interaction (the Zr–C3 linkage is only about 0.3 Å longer than the very short Zr–C1 σ bond) results in a very unusual coordination environment for carbon atom C3, featuring four strong bonding interactions to neighboring atoms in one plane [namely C3–C1 (1.324 (4) Å), C3–C4 (1.508 (5) Å), C3–Al (2.103 (3) Å), and C3–Zr (2.47 (1) Å)]. The bond angles around the planar tetracoordinate carbon atom C3 are 118.9 (2) (C1,C3,C4) 96.8 (3) (C4,C3,Al), 83.2 (3) (Al,C3,Zr), and 61.0 (6)° (C1,C3,Zr). In the central metallacyclic plane the Al···C4 and Al···C13 separations are 2.73 and 2.77 Å, respectively.

Complex **8a** exhibits an IR ν(C≡C) band at 2065 cm^{-1}. The ^{13}C NMR spectrum of **8a** features quarternary carbon resonances at δ 208.6 ($^2J_{CH}$ = 4 Hz, C1), 144.1, 142.8, 122.9, 114.8, and 110.9. One of the latter is to be attributed to the planar tetracoordinate carbon center. Complexes **8b,c** exhibit similar spectroscopic features.[8]

We have begun to use variations of this synthetic approach for preparing analogous compounds with other metal substituent and $M^1(\mu\text{-}X)M^2$ bridging ligand combinations and to actively investigate the chemistry of stable, isolable compounds containing planar tetracoordinate carbon.

Acknowledgment. Financial support from the Fonds der Chemischen Industrie, the Krupp-Stiftung, the Deutsche Forschungsgemeinschaft, and the Volkswagen-Stiftung is gratefully acknowledged.

Registry No. 6, 12636-72-5; **7a**, 17439-66-6; **7b**, 136408-15-6; **7c**, 136408-16-7; **8a**, 136408-17-8; **8b**, 136408-18-9; **8c**, 136408-19-0.

Supplementary Material Available: For **8a**, full listings of bond distances, bond angles, anisotropic thermal parameters, and atomic coordinates and isotropic thermal parameters (10 pages); a table of structure factors (36 pages). Ordering information is given on any current masthead page.

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[5] Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

[6] Kukina, G. A.; Porai-Koshits, M. A.; Sadikov, G. G.; Shevchenko, Y. N.; Esaulenko, A. N. *Koord. Khim.* **1986**, 1279.

[7] Kumar, P. N. V. P.; Jemmis, E. D. *J. Am. Chem. Soc.* **1988**, *110*, 125.

[8] **8b**: 0.8 g isolated (52%), mp = 121 °C dec; ^{13}C NMR (benzene-d_6) δ 197.7, 152.0, 106.9, 100.5 (quart C), 107.2 (Cp), 43.3, 32.6 (CH), 32.1, 31.4, 27.9, 26.8, 25.9, 25.2 (CH_2), 23.9 (CH_3), −6.4 ($AlMe_2$); IR (KBr) ν 2065 (C≡C), 1612 (C=C) cm^{-1}. **8c**: 1.2 g isolated (83%), mp = 105 °C dec; ^{13}C NMR (benzene-d_6) δ 224.0, 162.6, 141.6, 100.4 (quart C), 106.7 (Cp), 26.7 (CH_3), 3.3, −0.42 (2 × $SiMe_3$), −1.4 ($AlMe_2$); IR (KBr) ν 2003 (C≡C), 1563 (C=C) cm^{-1}.

Conformational Analysis of Phenylpentamethyldisilane and Related Compounds As Studied by Free-Jet Laser Spectroscopy[1]

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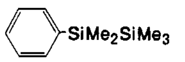
Received July 17, 1991

Summary: Conformational studies of phenylpentamethyldisilane (**1**) and related cyclic aryldisilanes by using free-jet laser spectroscopy and force-field calculations revealed that, in the preferred ground-state conformation of **1**, the Si–Si bond was perpendicular to the benzene ring plane, compatible with remarkable stereoelectronic effects on the absorption and fluorescence spectra of aryldisilanes.

Intriguing electronic properties of aryldisilanes have been demonstrated by means of UV, CT, and photoelectron spectroscopy.[2] For instance, phenylpentamethyldisilane (**1**) and 1-(trimethylsilyl)-1-methyl-2,3-benzo-1-silacyclopentane (**2**) showed intense absorption (^1L_a) maxima at around 230 nm, which are significantly longer than the usual maxima for substituted benzenes, while no



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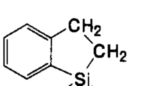

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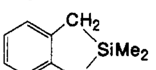

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[1] Chemistry of Organosilicon Compounds. 277.

[2] (a) Sakurai, H.; Tasaka, S.; Kira, M. *J. Am. Chem. Soc.* **1972**, *94*, 9285. (b) Bock, H.; Alt, H. *J. Am. Chem. Soc.* **1970**, *92*, 1569. (c) Sakurai, H.; Kira, H. *J. Am. Chem. Soc.* **1974**, *96*, 791. (d) Sakurai, H.; Kira, M. *J. Am. Chem. Soc.* **1975** *97*, 4879. (e) Pitt, C. G.; Carey, R. N.; Toren, E. C., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 3806. (f) Pitt, C. G.; Bock, H. *J. Chem. Soc., Chem. Commun.* **1972**, 28. For a review, see: Sakurai, H. *J. Organomet. Chem.* **1980**, *200*, 261.

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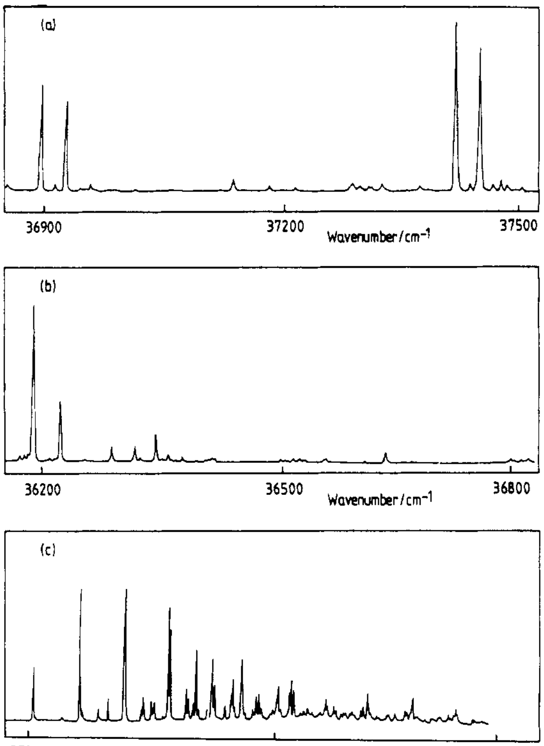
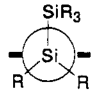
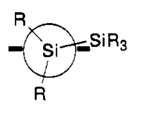


Figure 1. MPI spectra of jet-cooled 1 (a), 2 (b), and 3 (c).

characteristic ^1L_a band was observed for 1,1,2,2-tetramethyl-3,4-benzo-1,2-disilacyclopentane (**3**).[2a] Concerning the dihedral angle between a silicon–silicon bond and a benzene ring plane, **2** is fixed in the approximately perpendicular conformation A, while **3** is in the nearly in-plane conformation B. Stereoelectronic σ–π conjugation between a silicon–silicon σ orbital and a benzene pπ orbital would obviously be responsible for determining the electronic properties of aryldisilanes. On the basis of the similarity of the UV spectra between **1** and **2**, the preferred conformation of **1** has been suggested to be A in the ground state. Contrary to this argument, Shizuka et al. have recently assumed that **1** occupies preferably the in-plane conformation B in both the ground and excited states, in order to explain the unusual dual-fluorescence phenomena,[3] while we have proposed the orthogonal intramolecular charge-transfer (OICT) mechanism as another model,[4] which demands the conformation A in the ground state to obtain the largest overlap between the Si–Si σ and the benzene pπ orbitals and the conformation B in the CT excited state to minimize the energy; the latter model is closely related to the TICT mechanism in *p*-(dimethylamino)benzonitrile and sudden polarization in the $^1(\pi\pi^*)$ states of olefins. In this context, it is desirable to determine the preferred conformations of **1** in both the ground and excited states on the other experimental bases.



A



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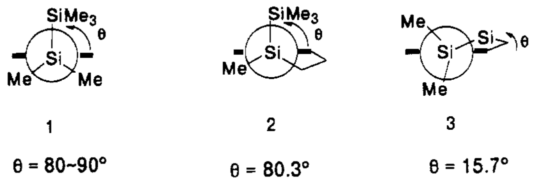

Figure 2. Dihedral angles between the Si–Si bond and the benzene ring plane at the MM2 optimized geometries of **1**–**3**.

By using free-jet laser spectroscopy and force-field calculations for **1** and related cyclic aryldisilanes **2** and **3**, the preferred rotational conformation of **1** was revealed unequivocally to be A in the ground state.[4] Free-jet laser spectroscopy has recently been shown as an effective means to analyze stable conformations and the number of various alkyl- and methoxy-substituted aromatic molecules at a temperature of nearly absolute zero.[5,6] During the course of our study, Teh et al., reported a related study on jet-cooled silylbenzenes, including **1**, but without detailed analysis of the preferred conformation.[7]

The multiphoton ionization (MPI) spectrum for S_1–S_0 or jet-cooled **1** is shown in Figure 1a. The spectrum displayed two intense origins at 36 897 and 36 932 cm^{-1}, with a 35-cm^{-1} spacing. Intense transition bands were also observed at 531 cm^{-1} higher energy from the origins. The progression band is tentatively assigned to a benzene ring 6b mode, since the 6b frequency of alkylbenzenes usually falls around 530 cm^{-1}.[6a] Similarly, the cyclic phenyldisilane **2** showed two intense origins with a 37-cm^{-1} spacing in the MPI spectrum (Figure 1b). The spectral similarity between **1** and **2** is obvious, whereas no satisfactory attribution is made of the 35-cm^{-1} spacing. Missing the 6b band in **2** may be attributed to the symmetry difference between **1** and **2**.

On the other hand, the MPI spectrum of **3** showed remarkable dissimilarity in the features from those of **1** and **2**, as shown in Figure 1c. In contrast to the intense 0_0^0 transition observed for **1** and **2**, a low-frequency mode was built on a weak origin transition at 35 811 cm^{-1} in **3**, with an energy level spacing of 55 cm^{-1}. Although the complexity of the molecule precludes the possibility of a comprehensive interpretation of the spectrum, the low-frequency mode may be ascribed to a torsional motion about the C_{ipso}–Si bond or a puckering vibration of the disilacyclopentane ring. Similar torsional progressions have been observed for α-methylstyrene, 9-phenylanthracene, biphenyl, and 9-(2-naphthyl)anthracene.[8] The torsional motion in **3** may involve a vibration directed toward

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(3) (a) Shizuka, H.; Obuchi, H.; Ishikawa, M.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1981**, 405. (b) Shizuka, H.; Sato, Y.; Ishikawa, M.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1982**, 439. (c) Shizuka, H.; Sato, Y.; Ueki, Y.; Ishikawa, M.; Kumada, M. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 341. (d) Shizuka, H.; Obuchi, H.; Ishikawa, M.; Kumada, M. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 383. (e) Shizuka, H.; Okazaki, K.; Tanaka, M.; Ishikawa, M.; Sumitani, M.; Yoshihara, K. *Chem. Phys. Lett.* **1985**, *113*, 89. (f) Hiratsuka, H.; Mori, Y.; Ishikawa, M.; Okazaki, K.; Shizuka, H. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 1665.

(4) Sakurai, H.; Sugiyama, H.; Kira, M. *J. Phys. Chem.* **1990**, *94*, 1837. Shizuka et al. have assigned the longer wavelength emission of the dual fluorescence of aryldisilanes to a CT excited state (2pπ^*,3dπ(Si) state), where the disilanyl group and the benzene π system work as an electron acceptor and an electron donor, respectively.[2] In contrast to this, the OICT mechanism involves a $\sigma\pi^*$ state as a CT excited state, where the donor–acceptor relationship is opposite to that of Shizuka's model.

(5) Seeman, J. I.; Secor, H. V.; Breen, P. J.; Grassian, V. H.; Bernstein, E. R. *J. Am. Chem. Soc.* **1989**, *111*, 3140 and references cited therein.

(6) (a) Hopkins, J. B.; Powers, D. E.; Smalley, R. E. *J. Chem. Phys.* **1980**, *72*, 5039. (b) Hopkins, J. B.; Powers, D. E.; Mukamel, S.; Smalley, R. E. *J. Chem. Phys.* **1980**, *72*, 5049. (c) Oikawa, A.; Abe, H.; Mikami, N.; Ito, M. *J. Phys. Chem.* **1984**, *88*, 5180. (d) Yamamoto, S.; Okuyama, K.; Mikami, N.; Ito, M. *Chem. Phys. Lett.* **1986**, *125*, 1.

(7) Teh, C. K.; Sipior, J.; Fink, M.; Sulkes, M. *Chem. Phys. Lett.* **1989**, *158*, 351.

(8) (a) Seeman, J. I.; Grassian, V. H.; Bernstein, E. R. *J. Am. Chem. Soc.* **1988**, *110*, 8542. (b) Werst, D. W.; Gentry, W. R.; Barbara, P. F. *J. Phys. Chem.* **1985**, *89*, 729. (c) Werst, D. W.; Brearly, A. M.; Gentry, W. R.; Barbara, P. F. *J. Am. Chem. Soc.* **1987**, *109*, 32. (d) Im, H.-S.; Bernstein, E. R. *J. Chem. Phys.* **1988**, *88*, 7337. (e) Murakami, J.; Ito, M.; Kaya, K. *J. Chem. Phys.* **1981**, *74*, 6505.

achieving a better σ(SiSi)–π overlap, which is restricted by the cyclic structure.

Comparison of the MPI spectra of **1**–**3** leads us to the conclusion that **1** prefers the perpendicular conformation A at low temperatures.

The dihedral angles between an Si–Si bond and a benzene ring plane at the most stable conformations were estimated by MM2 force-field calculations for **1**–**3**, as shown in Figure 2.[9] The MM2 calculations for **1** showed a shallow potential energy minimum at around A, together with another minimum at around B that was 1.3 kcal/mol higher in energy than A. The rotational barrier around the C_{ipso}–Si bond of **2** was calculated to be 1.5 kcal/mol, suggesting smooth rotation about the bond at room temperatures.

In conclusion, the present results are compatible with remarkable stereoelectronic effects on the absorption spectra of aryldisilanes as well as with the OICT model for the CT excited state of **1**.

Registry No. **1**, 1130-17-2; **2**, 40662-25-7; **3**, 40662-22-4.

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(9) Frierson, M. R.; Imam, M. R.; Zalkow, V. B.; Allinger, N. L. *J. Org. Chem.* **1988**, *22*, 5248.

Stereoelectronic Control of Electron Transfer in the Oxidative Addition of $[py(dmgH)_2Co^I]^-Na^+$ to Carbohydrate Secondary Iodides

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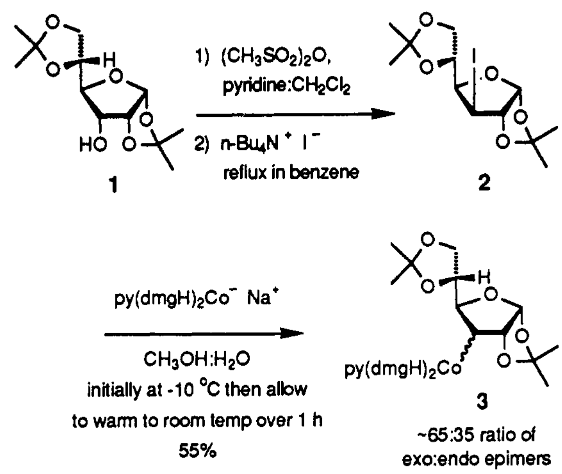
Received July 23, 1991

Summary: The relative rates of oxidative addition of secondary carbohydrate iodides **2**, **5**, and **7** with $[py(dmgH)_2Co^I]^-$, to form mixtures of diastereomeric alkyl cobaloximes **3** and **8**, are consistent with steric inhibition of the electron-transfer step. On the basis of these and previously reported observations, a unified mechanism for oxidative addition is proposed.

Organocobalt complexes have recently received attention in synthetic organic radical chemistry.[2,3] Organocobalt complexes can be formed by the oxidative addition of Co(I) complexes to alkyl, aryl, and vinyl halides. For such two-electron oxidative additions several mechanisms can be envisioned,[4] including (1) three-center cis addition, (2) S_N2 addition, (3) atom abstraction of halogen by one metal center followed by combination of the carbon-centered radical with another metal center, (4) inner-sphere electron transfer followed by caged radical-pair combination, (5) radical chains, and (6) outer-sphere electron transfer followed by combination of free carbon-centered radicals with a metal center. From the perspective of synthetic organic chemistry, it is usually adequate to distinguish between concerted mechanisms (1 and 2) and stepwise mechanisms (3–6), since such a simple distinction will cover most synthetically important aspects of stereochemistry and structure–reactivity relationships. Nevertheless, other more detailed aspects of reaction mechanism could have important consequences in using synthetic reactions in a predictable fashion. In this paper we report just such a case involving stereoelectronic control of electron transfer into carbon–halogen bonds.

Scheme I



We have been using alkylcobaloximes, $RCo^{III}(dmgH)_2py$ (dmgH = dimethylglyoxime monoanion; py = pyridine), for the development of new synthetic organic methodology.[2] Alkylcobaloximes are usually formed by the oxidative addition of $[py(dmgH)_2Co^I]^-$ to alkyl halides. In 1969 Schrauzer reported that the oxidative addition of $[py(dmgH)_2Co^I]^-$ with simple primary and secondary alkyl halides proceeded by an S_N2 mechanism.[5] This conclusion

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(1) Fellow of the Alfred P. Sloan Foundation, 1987–1989.

(2) (a) Branchaud, B. P.; Meier, M. S.; Choi, Y. *Tetrahedron Lett.* **1988**, *29*, 167. (b) Branchaud, B. P.; Meier, M. S. *Tetrahedron Lett.* **1988**, *29*, 3191. (c) Branchaud, B. P.; Choi, Y. L. *Tetrahedron Lett.* **1988**, *29*, 6037. (d) Branchaud, B. P.; Yu, G.-X. *Tetrahedron Lett.* **1988**, *29*, 6545. (e) Branchaud, B. P.; Choi, Y. L. *J. Org. Chem.* **1988**, *53*, 4638. (f) Branchaud, B. P.; Meier, M. S. *J. Org. Chem.* **1989**, *54*, 1320.

(3) (a) Bhandal, H.; Pattenden, G.; Russell, J. J. *Tetrahedron Lett.* **1986**, *27*, 2299. (b) Patel, V. F.; Pattenden, G.; Russell, J. J. *Tetrahedron Lett.* **1986**, *27*, 2303. (c) Patel, V. F.; Pattenden, G. *Tetrahedron Lett.* **1987**, *27*, 1451. (d) Coveney, D. J.; Patel, V. F.; Pattenden, G. *Tetrahedron Lett.* **1987**, *28*, 5949. (e) Patel, V. F.; Pattenden, G. *J. Chem. Soc., Chem. Commun.* **1987**, 871. (f) Bandaranayke, W. M.; Pattenden, G. *J. Chem. Soc., Chem. Commun.* **1988**, 1179. (g) Bhandal, H.; Pattenden, G. *J. Chem. Soc., Chem. Commun.* **1988**, 1110. (h) Pattenden, G. *Chem. Soc. Rev.* **1988**, *17*, 361. (i) Gill, G. B.; Pattenden, G.; Reynolds, S. J. *Tetrahedron Lett.* **1989**, *30*, 3229. (j) Bhandal, H.; Patel, V. F.; Pattenden, G.; Russell, J. J. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2691. (k) Patel, V. F.; Pattenden, G. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2703. (l) Bhandal, H.; Howell, A. R.; Patel, V. F.; Pattenden, G. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2709. (m) Coveney, D. J.; Patel, V. F.; Pattenden, G.; Thompson, D. M. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2721. (n) Ghosez, A.; Gobel, T.; Giese, B. *Chem. Ber.* **1988**, *121*, 1807. (o) Baldwin, J. E.; Li, C. S. *J. Chem. Soc., Chem. Commun.* **1987**, 166. (p) Baldwin, J. E.; Li, C. S. *J. Chem. Soc., Chem. Commun.* **1988**, 261. (q) Baldwin, J. E.; Moloney, M. G.; Parsons, A. F. *Tetrahedron* **1990**, *46*, 7263. (r) Scheffold, R. *Stud. Org. Chem.* **1987**, *30*, 275. (s) Busato, S.; Tinembart, O.; Zhang, Z. D.; Scheffold, R. *Tetrahedron* **1990**, *46*, 3155. (t) Scheffold, R. *Pure Appl. Chem.* **1987**, *59*, 363.

(4) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 279–322.

(5) Schrauzer, G. N.; Deutsch, E. *J. Am. Chem. Soc.* **1969**, *91*, 3341.

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