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John R. Fritch and K. Peter C. Vollhardt

June 1980

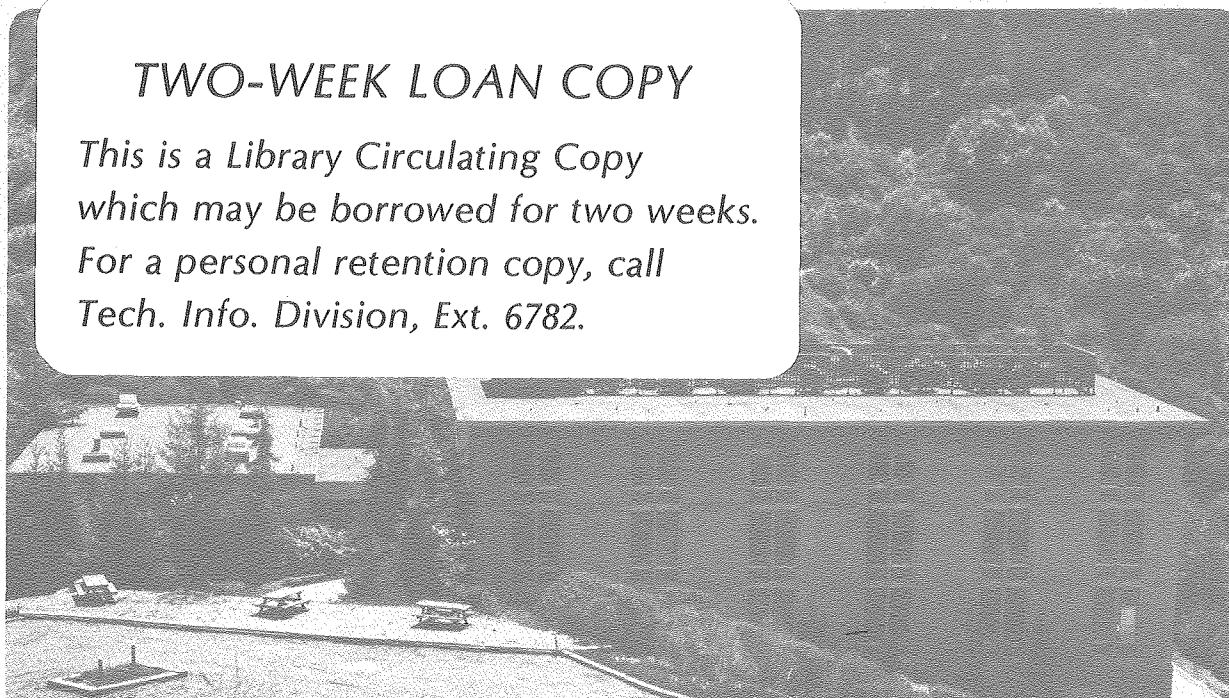
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Biscarbyne Clusters by Alkyne Cleavage: A General Reaction^[**]

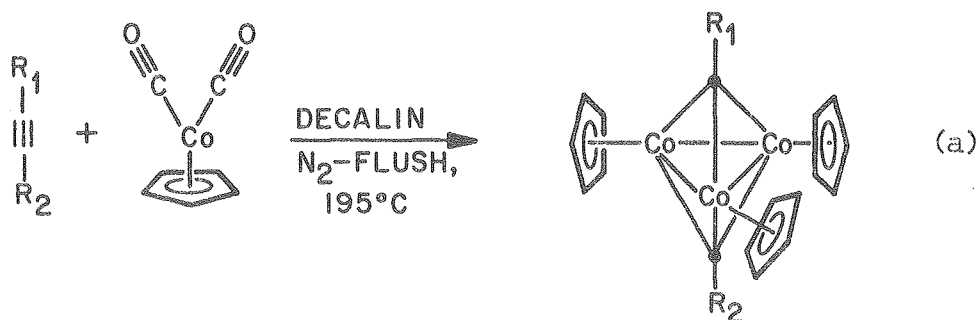
By John R. Fritch and K. Peter C. Vollhardt^[*]

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Surface carbyne species have recently been implicated in the H-D exchange of polymethylcycloalkanes mediated by cobalt films,^[1] the isomerization of saturated hydrocarbons on iridium catalysts,^[2] the interaction of acetylene and ethylene with platinum, nickel, and rhodium single crystals,^[3] and the hydrogenation of carbon monoxide (Fischer-Tropsch reaction) on heterogeneous systems.^[4] We describe a general synthesis and preliminary physical and chemical properties of biscarbyne clusters prepared by a conceptually most simple route, the direct cleavage of alkynes. Biscarbyne clusters, particularly those derived from multiple cleavage of oligoynes, apart from their novelty and potential application to organic synthesis, have excellent potential to serve as suitable substrates on which to study surface-homogeneous cluster analogies.^[5]

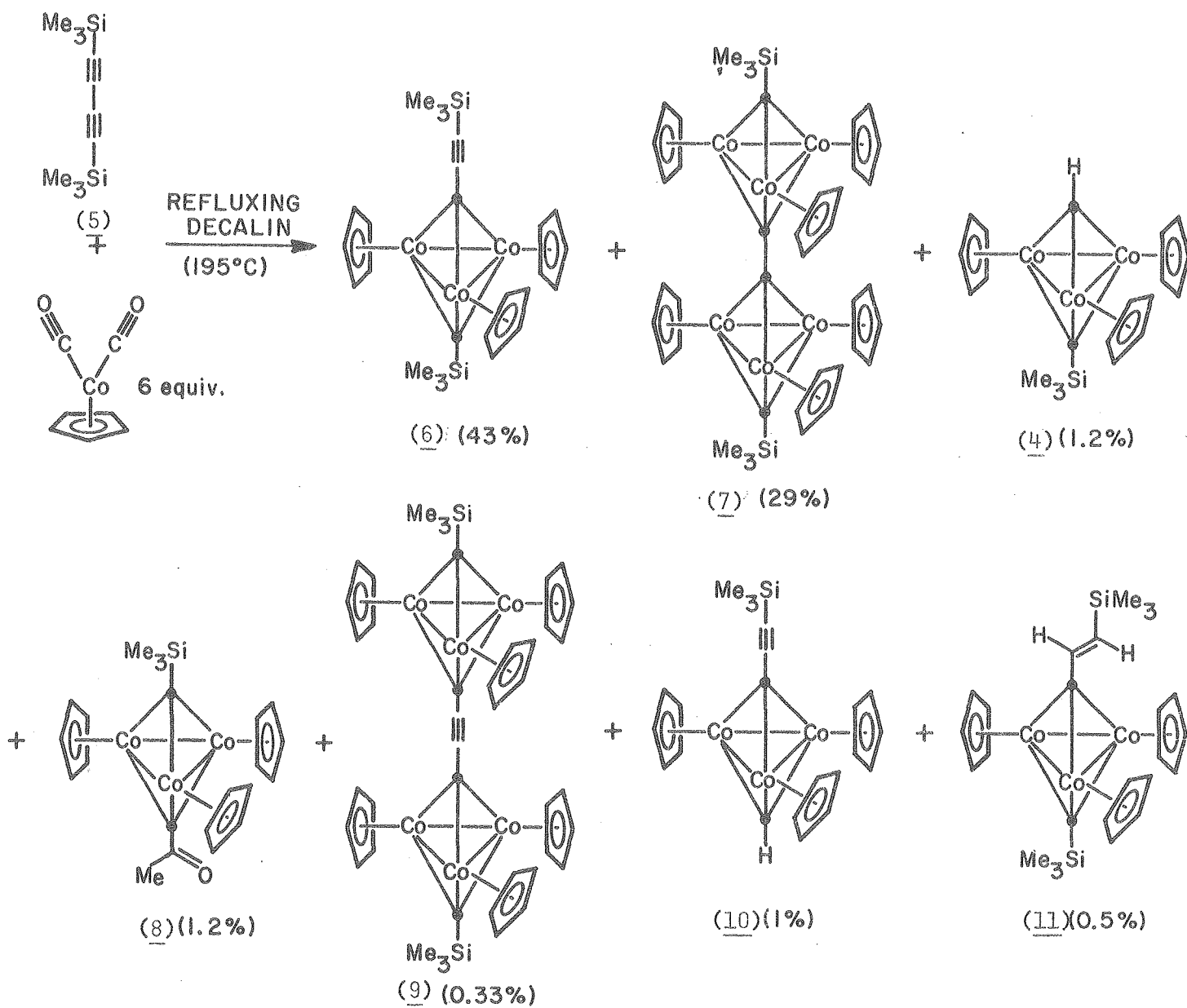
We^[6] have found that $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$, which ordinarily functions as a mediator of alkyne oligomerizations to furnish catalytic and stoichiometric products (e.g. benzenes, and complexed cyclopentadienones and cyclobutadienes)^[7] assembles a trinuclear $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}]_3$ cluster which inserts into alkyne functions



- (1) $R_1 = R_2 = \text{C}_6\text{H}_5$ (72%)
- (2) $R_1 = R_2 = \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ (56%)
- (3) $R_1 = R_2 = \text{CO}_2\text{CH}_3$ (16%)
- (4) $R_1 = \text{Si}(\text{CH}_3)_3$; $R_2 = \text{H}$ (32%)

with remarkable ease according to equation (a). Thus, when a solution of diphenylacetylene and $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ (3 equiv.) in decalin is slowly added (syringe pump) to boiling and nitrogen flushed decalin over 24h only 9% of the

ordinarily expected tetraphenylcyclobutadiene cyclopentadienyl cobalt^[8] is isolated on alumina chromatography. The major product (72%) is the biscarbyne cluster (1).^[9] In similar fashion hydrogen, alkyl, silyl, and carbomethoxy

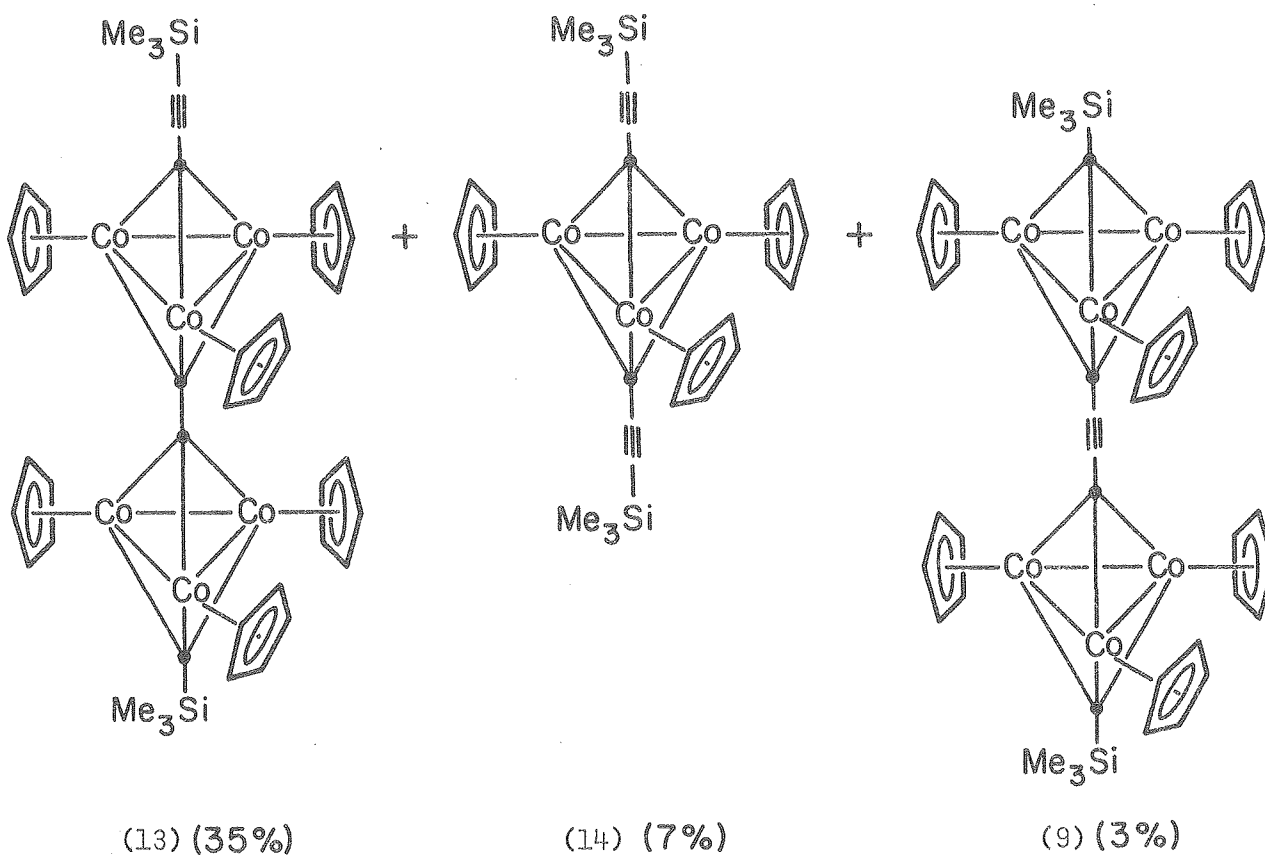


functionalized derivatives (2)-(4) may be isolated.^[9] This finding is important in view of the lack of generality of the many reactions of transition metals with organic substrates. In the cleavage of trimethylsilylated alkynes traces of other clusters are observed derived from acetylide coupling and decoupling, hydrolysis, and dimerization processes. For example, complete analysis of all chromatographable products from the conversion of bis(trimethylsilyl)butadiyne (5) with six equivalents of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ reveals seven clusters (4) and (6)-(11)! It should be noted that the "multiple decker" sandwich (7) is formed despite the considerable steric crowding in the system. Compounds (4) and (9) most likely arise via metathesis of (5) to trimethylsilylacetylene and bis(trimethylsilyl)butatriyne (12) (or their equivalents) in the coordination sphere of cobalt. A control experiment showed that (7) is an unlikely source of (4) via cleavage of the carbidobridge under the reaction conditions. Ketone (8) may be thought of as a hydrolysis product of (6) and cluster (10) is derived from (6) by protodesilylation under the reaction conditions (vide infra). The formation of (11) points to the presence of 1,4-bis(trimethylsilyl)-1, 3-butenyne in the reaction mixture, possibly derived by dimerization of trimethylsilylacetylene.^[10]

A similar array of products is obtained in the analogous reaction of bis(trimethylsilyl)hexatriyne (12), but again the major components of the reaction mixture are the singly inserted (14), and the "multiple deckers" (9) and (13).^[9]

Treatment of (6) with 1% KOH-EtOH gave quantitative monodesilylation to the unstable terminal acetylene (15),^[9] whereas the action of $\text{n-Bu}_4\text{N}^+\text{F}^-$ in hot THF led to complete desilylation to the unsilylated analog of (6), compound (16).^[9]

The parent biscarbyne $[\mu_3\eta^1\text{-HC}]_2[(\eta^5\text{-C}_5\text{H}_5)\text{Co}]_3$ (17) is available from (4) by protodesilylation $[\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{CH}_3)_3]^+\text{F}^-$, DMSO, 105°C, 6h, 87%.^[9] Remarkably,



instant H-D exchange at the carbyne carbon is observed^[9] when (4) or (17) are exposed to $\text{CF}_3\text{CO}_2\text{D}-\text{C}_6\text{D}_6$ (1:1, 25°C, deep green solution) in an NMR tube under conditions which lead to neither deuterodesilylation nor deuterium incorporation into the cyclopentadienyl ligands (1h).^[11] In contrast, cluster (1) is inert to alcoholic HCl, but reacts with hot $\text{CF}_3\text{SO}_3\text{H}$ to furnish benzene and toluene. On the other hand, when (4) is exposed to n-butyllithium-TMEDA (THF, 25°C, 30 min.) followed by D_2O -work-up unchanged (4) is isolated.

To test for the potential of carbyne exchange, (1) was heated in boiling decalin with excess (4 equiv.) of p-ditolylacetylene^[12] for 39d. Only traces of 1, 2-diphenyl-3, 4-ditolyl- and tetratolylcyclobutadiene cyclopentadienyl cobalt were recovered, in addition to diphenylacetylene (21%), starting cluster (74%), and ditolylacetylene (74%). Biscarbynes may act as, or be precursors of, catalytically active species. Heating (4) with 1-heptene in a stainless steel bomb to 200°C for 36h in the presence of CO (400 psi) and H_2 (800 psi) gave

1-octanal, 1-octanol, 2-methylheptanal, and 2-methylheptanol with respective turn-overs of 30, 6.8, 15.4, and 5.0 per equivalent of cobalt. Starting (4) was completely consumed.

The spectral data^[9] of the reported biscarbynes are unusual, revealing the profoundly deshielding effect and the strong electron releasing ability of the cluster unit.^[13]

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- [8] M.D. Rausch, R.A. Genetti, J. Org. Chem. 35, 3888 (1970).
- [9] All new compounds gave satisfactory analytical data. Compound (1): dark purple prisms; sublimation 200°C, 10^{-3} Torr; mp 256-257°C; m/e 550 (M^+ 100%), 370 (27%), 247 (20%), 189 (96%), 124 (30%); NMR δ (CCl_4)

8.13 (dd, $J=1.7\text{Hz}$, 7.8 Hz, 4H), 7.37 (m, 6H), 4.33 (s, 15H);
 $^{13}\text{C-NMR}$ δ [CDCl_3 , $\text{Cr}(\text{acac})_3$] 334.6, 167.3, 127.4, 126.7, 125.3, 85.2;
 (2): purple needles, mp 115.5–116°C; m/e 510 (M^+ , 78%), 508 (40%),
 370 (100%), 247 (38%), 189 (87%); NMR δ (C_6D_6) 4.97 (t, $J=8.0\text{Hz}$, 4H), 4.33
 (s, 15H), 2.61 (q, $J=7.4\text{Hz}$, 4H), 1.89 (sex, $J=7.0\text{Hz}$, 4H), 1.26 (t, $J=7.0\text{Hz}$,
 6H); (3): dark purple needles, mp 244–247°C; m/e 514 (M^+ , 41%), 189
 (100%); NMR δ (C_6D_6) 4.49 (s, 15H), 3.96 (s, 6H); IR (CHCl_3) ν_{CO}
 1664 cm^{-1} ; (4): dark purple needles, sealed capillary (N_2) sublimation at
 250–310°C, then dec.; m/e 470 (M^+ , 100%), 370 (54%), 247 (28%), 189
 (85%); NMR δ (C_6D_6) 18.25 (s, 1H), 4.42 (s, 15H), 0.83 (s, 9H); (6): $^{13}\text{C-NMR}$
 δ (CDCl_3) 373.4, 279.4, 127.5, 127.0, 83.9, 4.00, 0.76; (7): red-bronze
 crystals, dec p 400°C; m/e 938 (M^+ , 22%), 749 (M-Cp₂Co, 12%), 189 (100%);
 NMR δ (CS_2) 4.63 (s, 30H), 0.94 (s, 18H); (8): red purple needles, dec
 p 399°C; m/e 512 (M^+ , 19%), 370 (1%), 247 (12%), 189 (100%); NMR δ
 (CCl_4) 4.43 (s, 15H), 3.09 (s, 3H), 0.78 (s, 9H); IR (CHCl_3) ν_{CO} 1618
 cm^{-1} ; 9: maroon crystals, dec p 392°C; m/e 962 (M^+ , 70%), 773 (M-Cp₂Co,
 8%), 189 (100%); NMR δ (CCl_4) 4.54 (s, 30H), 0.83 (s, 18H); (10):
 red-purple flakes, mp 213–217°C; m/e 494 (M^+ , 49%), 370 (14%), 271 (25%),
 247 (49%), 189 (100%), 124 (22%); NMR δ (C_6D_6) 18.60 (s, 1H) 4.44
 (s, 15H), 0.52 (s, 9H); IR (CHCl_3) $\nu_{\text{C}\equiv\text{C}}$ 2062 cm^{-1} ; (11): purple needles, mp
 178–180°C; m/e 568 (M^+ , 69%), 370 (16%), 247 (14%), 189 (100%); NMR
 δ (C_6D_6) 9.46 (d, $J=19.0\text{Hz}$, 1H), 6.62 (d, $J=19.0\text{Hz}$, 1H), 4.35 (s, 15H),
 0.78 (s, 9H), 0.44 (s, 9H); (13): red-bronze flakes, dec p 393°C; m/e
 962 (M^+ 44%), 773 (M-Cp₂Co, 21%), 189 (100%), NMR δ (CDCl_3) 4.68 (s, 15H),
 4.62 (s, 15H), 0.92 (s, 9H), 0.53 (s, 9H); IR (KBr) $\nu_{\text{C}\equiv\text{C}}$ 2069 cm^{-1} ;
 (14): purple crystals, mp 161.5–165°C; m/e 590 (M^+ , 37%), 189 (100%);
 NMR δ (C_6D_6) 4.38 (s, 15H), 0.48 (s, 18H); IR (CHCl_3) $\nu_{\text{C}\equiv\text{C}}$ 2061 cm^{-1} ;

(15): purple flakes, dec p 102-116°C; m/e 494 (M^+ , 32%), 189 (100%); NMR $\delta(C_6D_6)$ 6.78 (s, 1H), 4.45 (s, 15H), 0.79 (s, 9H); IR ($CHCl_3$) ν_{CCH} 3300 cm^{-1} , $\nu_{C\equiv C}$ 2024 cm^{-1} ; (16): purple prisms, dec p 25°C; m/e 422 (M^+ , 45%), 271 (17%), 189 (100%); NMR $\delta(C_6D_6)$ 18.68 (s, 1H), 6.72 (s, 1H) 4.43 (s, 15H); IR ($CHCl_3$) ν_{CCH} 3295 cm^{-1} , $\nu_{C\equiv C}$ 2020 cm^{-1} ; (17): purple crystals, sublimation 160°C, 10^{-3} Torr; dec p 380-390°C; m/e 398 (M^+ , 64%), 370 (42%), 247 (45%), 189 (100%), 124 (10%); NMR $\delta(C_6D_6)$ 18.37 (s, 2H), 4.38 (s, 15H).

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