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COBALT METALLOCYCLES

IV [*]. RING OPENING OF COBALTACYCLOPENTADIENES BY ADDITION OF Si—H, S—H, N—H AND C—H TO THE DIENE MOIETY

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Summary

Cobaltacyclopentadiene complexes, $(\eta^5\text{-}C_5H_5)(PPh_3)(\overline{CoCR^1{=}CR^2CR^2{=}CR^1})$ (R^1, R^2 = Ph, Me, CO_2Me), reacted with R—H (RH: triethylsilane, thiocresol, dimethyl- and ethylene-thiourea, pyrrole, thiophene) to give diene complexes, $(\eta^5\text{-}C_5H_5)(\eta^4\text{-}HCR^1{=}CR^2CR^2{=}CR^1R)Co$, or uncomplexed, highly substituted butadiene derivatives, $HCR^1{=}CR^2CR^2{=}CR^1R$. The reaction with thiourea proceeded catalytically in the presence of excess of diphenylacetylene although turn-over of the catalyst was small.

Introduction

Cobaltacyclopentadienes are of greater advantage than other metallocyclopentadienes because a variety of substituents can be introduced on the metallocyclopentadiene ring [1,2a]. Recent studies have shown the utility of these cobaltacyclopentadienes in the stoichiometric synthesis of homo- and heterocyclic organic compounds [2]. In these reactions the unsaturated reagent (X = Y) couples with the organic moiety of the cobaltheterocycle, forming cyclic compounds (eq. 1). We have also suggested the importance of eq. 1 in "$(\eta^5\text{-}C_5H_5)Co$" catalyzed cyclotrimerization of acetylenes [3a] and cocyclotrimerization of acetylenes with nitriles [3b,c]. Recent reports by Vollhardt et al. demonstrate a nice application of this principle to diacetylene systems [3d,e,f].

As a continuation of our studies on cobalt metallocycles, we have investigated the thermal transformation of cobaltacyclopentadiene complexes to cyclobutadiene complexes [4]. In one case, however, that of benzene which was used as solvent, a side reaction formed a trace amount of open-chain diene complex

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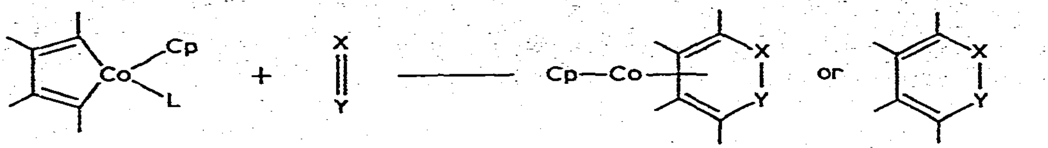
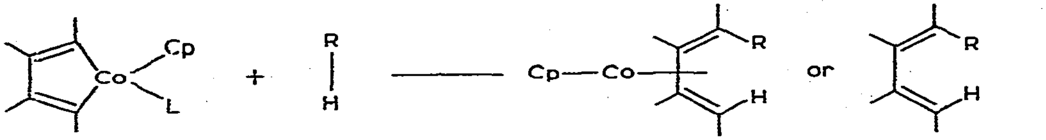
[*] For part III see ref. 4.



(1)



(2)

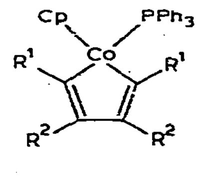
(Cp : η^5-C_5H_5 , L : PPh_3)

by addition to the 1,4-positions of the diene moiety (eq. 2, R = Ph). The addition of aryl-H to the diene moiety of the metallocycle became a predominant reaction when the aryl group was forced to stay near the reaction site, i.e., in the case of the η^5-benzylcyclopentadienyl complex [4]. These observations gave us a hint that some reagents, R—H, which have heteroatom(s) in R, might cleave the cobalt—carbon σ-bonds in a similar fashion and thereby enable us to utilize the organic moiety of the cobalt metallocycle in the generation of open-chain organic species. The heteroatom(s) in R was expected to interact with cobalt, thus keeping R—H near the reaction center. Details of this type of ring-opening reaction are reported here.

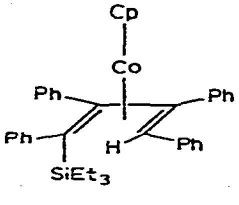
Results and discussion

Addition of triethylsilane

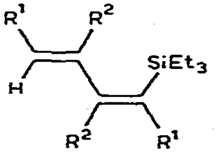
(η^5-Cyclopentadienyl)(triphenylphosphine)-2,3,4,5-tetraphenylcobaltacyclopentadiene (Ia) and triethylsilane reacted at 70°C to give a black crystalline complex, whose structure was determined by an X-ray analysis to be (η^5-cyclopentadienyl)(η^4-1-*anti*-triethylsilyl-1,4-*syn*-diphenyl-2,3-diphenylbutadiene)-cobalt (IIa) [5]. At 120°C, the reaction gave a colorless, oily product of the composition $(PhC_2Ph)_2(Et_3SiH)$ (IIIa). Similarly, the reaction of (η^5-cyclopentadienyl)(triphenylphosphine)-2,5-diphenyl-3,4-dimethoxycarbonylcobaltacyclopentadiene (Ib) with triethylsilane at 120°C afforded a colorless oil of the com-



(Ia) R^1 = Ph, R^2 = Ph
(Ib) R^1 = Ph, R^2 = CO_2Me
(Ic) R^1 = Ph, R^2 = Me
(Id) R^1 = CO_2Me, R^2 = Me



(IIa)



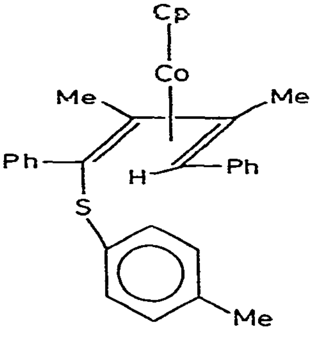
(IIIa) R^1 = Ph, R^2 = Ph
(IIIb) R^1 = Ph, R^2 = CO_2Ph

position $(PhC_2CO_2Me)_2(Et_3SiH)$ (IIIb). Based on the structure of IIa, compounds IIIa and IIIb were assigned the structures as shown.

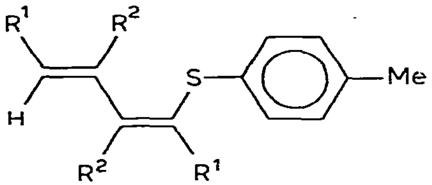
The other dienes and their complexes obtained in this study by the analogous reactions were tentatively assumed to have a configuration similar to that of IIIa and IIa.

Addition of a thiol

(η^5-Cyclopentadienyl)(triphenylphosphine)-3,4-dimethyl-2,5-diphenylcobaltacyclopentadiene (Ic) reacted with *p*-thiocresol to give a diene complex (IVc) at 70°C, whereas the free butadiene derivatives (Vb, Vd) were formed by the reaction of Ib and Id with *p*-thiocresol at 120°C.



(IVc)

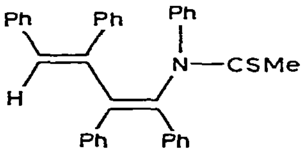


(Vb) $R^1 = Ph, R^2 = CO_2Me$

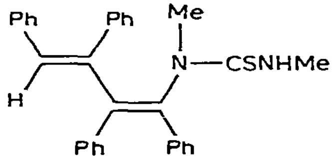
(Vd) $R^1 = CO_2Me, R^2 = Me$

Addition of thioacetanilide, dimethyl- and ethylene-thiourea

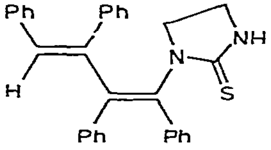
Thioacetanilide reacted with Ia at 70°C to give the free butadiene derivative (VIa). The formation of analogous compounds, VIIa and VIIIa, could be carried out catalytically when a ca. 15 fold excess of diphenylacetylene was added to the reaction system. Turnover of the catalyst (Ia) was about 4.



(VIa)



(VIIa)



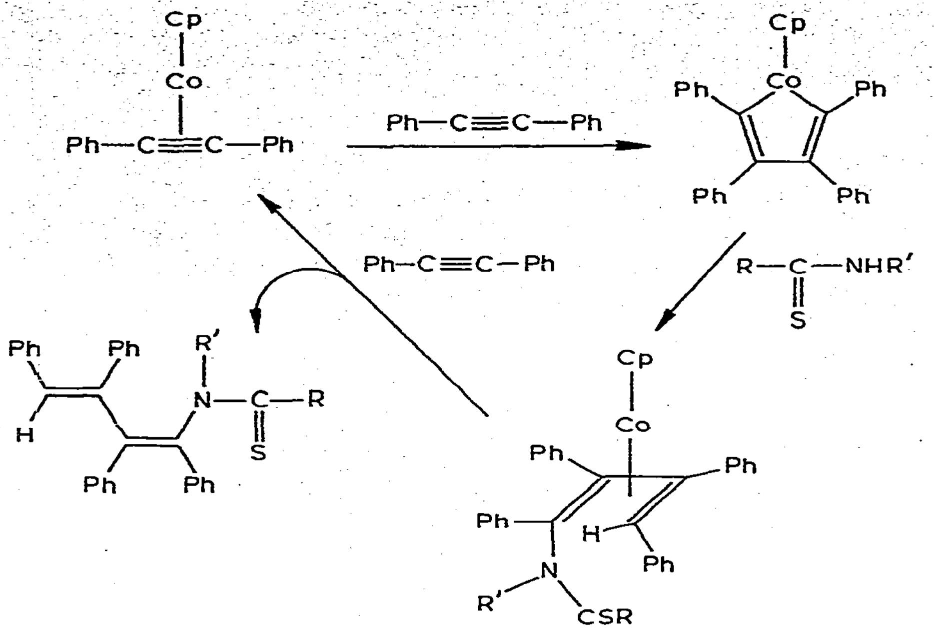
(VIIIa)

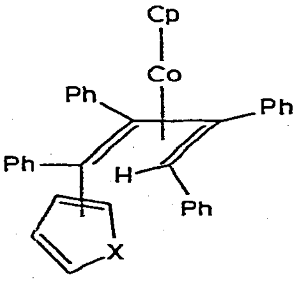
Since Ia is prepared from the monoacetylene complex and diphenylacetylene [1], the catalytic cycle may be written as shown in Scheme 1.

Addition of pyrrole and thiophene

Pyrrole and Ia reacted at 70°C to give black crystals of empirical formula $(C_5H_5)(PhC_2Ph)_2(C_4H_5N)Co$ (IXa). The IR spectrum of the complex showed a ν(NH) absorption at 3450 cm^{-1}, indicating that the pyrrole added to the diene moiety with its carbon atom. Thiophene also gave a similar product (Xa). Whether the attachment of these aromatic heterocycles to the diene is at their 2- or 3-position is not clear as yet.

SCHEME 1





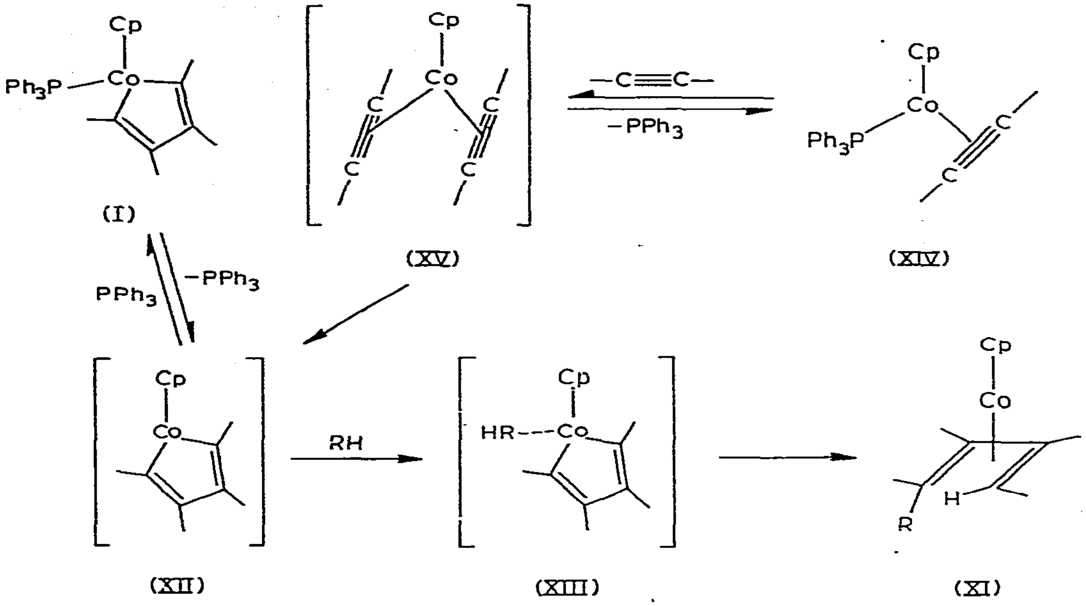
(IXa) X = NH

(Xa) X = S

Nucleophilic addition of pyrrole, thiophene, and related heterocyclic aromatics to cationic cyclohexadienyl complexes has been known to give neutral complexes of diene-substituted heterocycles [6]. In these nucleophilic reactions pyrrole adds at its 2-position to the cyclohexadienyl ring ca. 10^6 times faster than thiophene [6c]. These large difference in reactivity between pyrrole and thiophene were not observed in the present case, suggesting that their attack at cobaltacyclopentadienes has little nucleophilic character.

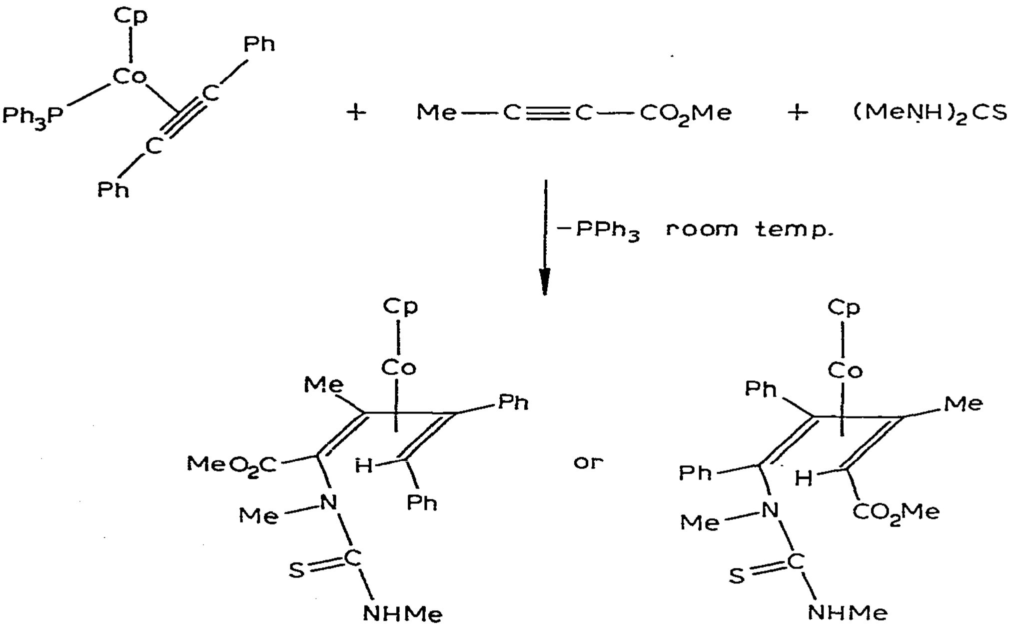
Previously, we have reported that cobaltacyclopentadienes (I) react with olefins to form cyclohexadienes and that the first step of the reaction is displacement of phosphine by olefin [7]. In the present ring-opening reaction, a similar reaction mechanism may be operative (Scheme 2). On heating I, a coordinatively unsaturated cobalt metallocycle (XII) may be formed. Heteroatom(s) in RH would play an important role by interacting with the coordina-

SCHEME 2



tively unsaturated cobalt atom thus formed and thereby supplying the active hydrogen to the reaction site (XIII). It was assumed that heating the reaction mixture was required primarily to remove the phosphine ligand from I.

Intermediate XII may be accessible by another route: XIV → XV → XII → I



(XIe)

TABLE 1

COBALT—DIENE COMPLEXES [a]

	Yield (%)	M.p. (dec.) (°C)	Analysis found (calcd.) (%)			PMR (in $CDCl_3$) (δ, ppm)		
			C	H	S or N	C_5H_5	H on the diene skelton	Others [c]
IIa	77	187—189	78.01 (78.49)	6.95 (6.93)		4.68	2.40	Si—C_2H_5 0.4—1.1(m)
IVc	31	155—156	75.45 (74.98)	5.89 (6.08)	S, 6.22 (6.67)	4.64	1.10	CH_3 2.16(s) 2.48(s) 2.72(s)
IXa	17	173—175	79.46 (81.16)	5.66 (5.52)	N, 2.41 (2.56)	4.68	1.56	Pyrrole [d] 5.90(m, 1H) 6.05(m, 1H)
Xa	30	174—175	78.12 (78.71)	5.24 (5.18)	S, 5.51 (5.68)	4.71	2.12	[e]
XIc	12	217—220	60.98 (60.38) [b]	5.70 (5.79)	N, 5.18 (5.12)	4.72	1.12	CH_3 2.38(s) N—CH_3 3.18(s), CO_2CH_3 3.30 (d, J 4 Hz) 2.73(s)

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[a] All the complexes gave reasonable mass spectra. [b] Contained 1/2 · CH_2Cl_2 as crystalizing solvent, which was confirmed by the PMR spectrum. [c] Absorptions by phenylprotons are omitted. [d] Other protons of pyrrole moiety were shaded by the phenyl absorptions. [e] Protons on the thiophene skelton were shaded by the phenyl absorptions.

has been the proposed reaction route in the formation of I from XIV and acetylene, which proceeded at room temperature [1]. If these hypotheses are correct, monoacetylene complex XIV should give diene complex XI at room temperature when being reacted with acetylene in the presence of R—H. This was successfully demonstrated in the case shown below:

Experimental

The characterizing data for the diene complexes and the free butadienes obtained are summarized in Tables 1 and 2.

All the reactions were carried out under nitrogen atmosphere. Melting points were uncorrected and determined on a Mitamura micro melting point apparatus. Proton NMR spectra were obtained using Varian HA-100 or JEOL-60 spectrometer in $CDCl_3$. IR spectra were obtained using a Shimazu IR-27G spectrometer.

For column chromatography, Sumitomo Activated Alumina KCG-30 was used.

Complexes Ia—Id and XIV were prepared as described previously [1].

Reaction of triethylsilane. To a solution of Ia (300 mg) in benzene (10 ml) was added triethylsilane (1 ml) and the mixture was heated at 70°C for 48 h in a sealed tube. The resulting dark solution was concentrated and chromatographed on alumina. A dark-brown band was elutated with 1/1 benzene/hexane. The solvent was evaporated under reduced pressure and hexane was added to give black crystals (220 mg) of IIa. When the initial reaction mixture was heated at 120°C for 168 h, most of the complex decomposed. Work-up by column chromatography gave a small yellow band of the cyclobutadiene complex, $(\eta^5\text{-}C_5H_5)(PhC_2Ph)_2Co$. A colorless product which was eluted with 1/3 benzene/hexane came out before the yellow cyclobutadiene complex band was collected. The solvent was evaporated under high vacuum to give viscous oil, IIIa.

Similarly, the colorless oil IIIb was obtained when triethylsilane was allowed to react with Ic in benzene at 120°C for 48 h and the resulting reaction mixture was chromatographed on alumina with elution by 1/1 benzene/dichloromethane.

Reaction of thiol. A solution of Ic (278 mg) and *p*-thiocresol (100 mg) in benzene (15 ml) was heated in a sealed tube at 70°C. After one week, the reaction mixture was concentrated and chromatographed on alumina. A brown-red band was eluted with 1/1 benzene/hexane. After the removal of the solvent, the residue was dissolved in hexane and cooled to give dark-brown crystals of IVc.

Similar reaction of Ib with thiocresol was carried out at 120°C for 24 h. Column chromatographic work-up gave colorless crystals of Vb.

The reaction of Id with thiocresol was accomplished at 140°C in toluene. The eluate from alumina column with dichloromethane was collected and the solvent was evaporated. From the hexane solution of the residue, colorless crystals of Vd were formed.

Reaction of thioacetanilide. A mixture of Ia (225 mg) and thioacetanilide (226 mg) in benzene (15 ml) was heated at 70°C in a sealed tube. After 30 h the mixture was concentrated and chromatographed on alumina. The eluate with benzene was concentrated and hexane was added to give colorless crystals of VIa.

TABLE 2

SUBSTITUTED BUTADIENES [a]

	Yield (%)	M.p. (°C)	Analysis found (calcd.) (%)			PMR (in $CDCl_3$) (δ, ppm)	
			C	H	N, S	H on the diene skelton	Others [b]
IIIa	87	[c]	86.47 (86.38)	7.69 (7.68)		[d]	Si—C_2H_5 0.5—1.0(m)
IIIb	44	[c]	71.15 (71.53)	7.32 (7.39)		[d]	Si—C_2H_5 0.5—1.0(m)
Vb	59	109—110	72.99 (72.95)	5.28 (5.44)	S, 7.29 (7.21)	7.82(s) ?	CO_2CH_3 3.72(s), 3.78(s) CH_3 2.11(s)
Vd	15	84—87	63.75 (63.73)	6.35 (6.29)		5.65(s)	CO_2CH_3 3.36(s), 3.85(s) CH_3 2.04(s) diene—CH_3 2.22(s), 2.28(s)
VIa	17	190—191	85.91 (86.11) [e]	6.25 (6.02)	N, 2.36 (2.39) S, 4.99 (5.47)	[d]	CO_2CH_3 3.54(s), 3.63(s) CH_3 2.46(s)
VIIa	[f]	185—186	80.88 (80.83)	6.17 (6.13)	N, 5.99 (6.08)	6.32(s)	CH_3 2.56(s) CH_3 3.02(d, J 4.2 Hz)
VIIIa	[g]	208—210	82.93 (82.80) [e]	6.12 (6.01)	N, 5.18 (5.22) S, 5.92 (5.97)	6.42(s)	—CH_2—CH_2— 2.0—3.2(m)

[a] All the compounds gave reasonable mass spectra. [b] Phenyl absorptions are omitted. [c] Viscous oil. [d] Shaded by the phenyl absorptions. [e] Solvated with C_6H_6. [f] Catalytic, turn over 3.8. [g] Catalytic, turn over 4.2.

Catalytic reactions of dimethyl- and ethylene-thiourea. A mixture of Ia (40 mg), diphenylacetylene (200 mg) and dimethylthiourea (130 mg) in benzene (15 ml) was heated at 70°C for 60 h. Concentrated reaction mixture was chromatographed on alumina. The column was washed throughly with benzene and then the eluate with dichloromethane was collected. Concentration of the eluate, followed by addition of hexane, gave colorless crystals of VIIa.

A similar reaction of ethylene thiourea was conducted in 2/1 benzene/ethanol solution. The fraction containing VIIIa was eluted with 5/1 dichloromethane/ tetrahydrofuran through an alumina column.

Reactions of pyrrole and thiophene. A solution of Ia (297 mg) and pyrrole (2 ml) in benzene (18 ml) was heated at 70°C for 15 h. Concentration and chromatography of the reaction mixture gave a brown band which was eluted with 1/1 benzene/hexane and a dark-brown band which was eluted with benzene. From the first brown band, unreacted Ia was recovered (46%). From the second dark-brown eluate, black crystals of IXa were obtained when the eluate was concentrated and hexane added.

Similar reaction of thiophene and chromatographic work-up on alumina yielded the yellow cyclobutadiene complex, $(\eta^5\text{-}C_5H_5)(PhC_2Ph)_2Co$ (13%), black crystalline Xa which was eluted with 1/1 benzene/hexane, and unreacted Ia (22%).

Formation of XIe from monoacetylene complex. To a benzene solution (40 ml) of (η^5-cyclopentadienyl)(diphenylacetylene)(triphenylphosphine)cobalt (200 mg) and dimethylthiourea (364 mg) was added methyl propiolate (0.1 ml) and the mixture was allowed to stand at room temperature for 2 days. The concentrated reaction mixture was chromatographed on alumina and a brown band was eluted with 10/1 dichloromethane/tetrahydrofuran. Concentration of the eluate and addition of hexane gave the red-brown crystalline complex XIe.

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