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PREPARATION OF THE CARBONYLCYCLOPENTADIENYLBIS(TRIMETHYLPHOSPHINE)COBALT(III) CATION AND ITS REACTIONS WITH NUCLEOPHILES

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Summary

The complexes $[C_5H_5Co(CO)(PMe_3)_2]X_2$ (X = BF_4, PF_6) have been prepared by carbonylation of $[C_5H_5Co(PMe_3)_2I]I$ in presence of silver ion. The carbonyl group is subject to nucleophilic attack by alcohols, amines and ammonia. New, stable alkoxycarbonyl $[C_5H_5Co(PMe_3)_2CO_2R]BF_4$ (R = Me, Et) and carbamoyl $[C_5H_5Co(PMe_3)_2CONHR]PF_6$ (R = H, Me, Et, $PhCH_2$) complexes have been prepared and characterised. The carbonyl group of the dication is readily displaced by polar solvents (DMF, DMSO, $MeNO_2$, MeCN) to give either $[C_5H_5Co(PMe_3)_2L]X_2$ (L = MeCN) or $[C_5H_5Co(PMe_3)_3]X_2$ (L = DMF, DMSO, $MeNO_2$). Reactions with other nucleophiles are discussed. The alkoxycarbonyl and carbamoyl complexes react with aqueous HBF_4 to regenerate the cationic carbonyl $[C_5H_5Co(CO)(PMe_3)_2]^{2+}$.

Introduction

Although it is now almost 15 years since the nucleophilic attack of alcohols and amines on metal carbonyls to give alkoxycarbonyl (L_nM—COOR) and carbamoyl (L_nM—CONHR) compounds was discovered, there have been relatively few such reports on complexes with M = Co. Alkoxycarbonylcobalt complexes have been prepared by the base-catalysed reaction of $[Co(CO)_3L_2]^+$ (L = PPh_3, $P(OPh)_3$) with alcohols [1] and by the reaction of cobalt corrins with ROH [2]. The nucleophilic attack of cobalt compounds behaving as Lewis bases on chloroformate esters to give complexes with Co—COOR bonds has also been described [1—4]. The only report of carbamoylcobalt complexes involves the

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reaction of $Co_2(CO)_8$ with secondary amines in the presence of triphenylphosphine to give $Co(CO)_3(PPh_3)CONR_2$ [5]. The subject of alkoxycarbonyl and carbamoyl complexes of transition metals has been reviewed by Angelici [6].

The present paper describes the preparation of the complexes $[C_5H_5Co(CO)(PMe_3)_2]X_2$ ($X = BF_4, PF_6$) and their reactions with nucleophiles.

Results and discussion

The complex $C_5H_5Co(CO)I_2$, first described by King [7] and Heck [8], reacts readily with trimethylphosphine at room temperature, the products being $[C_5H_5Co(PMe_3)_3]I_2$ (I) (the corresponding tetrafluoroborate $[C_5H_5Co(PMe_3)_3](BF_4)_2$ has already been reported [9]) and the new complex $[C_5H_5Co(PMe_3)_2I]I$ (II). With excess of the phosphine, I is formed exclusively but if two mol PMe_3 per mol $C_5H_5Co(CO)I_2$ are used the reaction is solvent dependent. In solvents in which II is soluble it rapidly reacts further to give I in stoicheiometric yield. In benzene, in which II is insoluble, it is the main product, together with a small amount of I from which it is easily separated by recrystallisation.

$$C_5H_5Co(CO)I_2 + 2\ PMe_3 \xrightarrow{C_6H_6} \underset{(II,\ 77\%)}{[C_5H_5Co(PMe_3)_2I]I} + \underset{(I,\ 6\%)}{[C_5H_5Co(PMe_3)_3]I_2} \qquad (1)$$

Complex II forms dark yellow-brown crystals which after a further recrystallisation appear almost black. It is air-stable and soluble in polar organic solvents.

$C_5H_5Co(CO)I_2$ reacts readily with one mol of triphenylphosphine to give the complex $C_5H_5Co(PPh_3)I_2$ [7a]. With one mol of trimethylphosphine, however, this reaction leads to the stoicheiometric amount of II and unchanged $C_5H_5Co(CO)I_2$.

Treatment of complex II with carbon monoxide in the presence of $AgBF_4$ in acetone solution leads to $[C_5H_5Co(CO)(PMe_3)_2](BF_4)_2$ (III). The corresponding PF_6 salt $[C_5H_5Co(CO)(PMe_3)_2](PF_6)_2$ (IV) is analogously prepared and is far more easily isolated in high yield. It is also preferable for further reactions because of its better solubility.

$$\mathrm{II} + CO + 2\ AgX \rightarrow [C_5H_5Co(CO)(PMe_3)_2]X_2 + 2\ AgI \qquad (2)$$

$$\begin{array}{l}(\mathrm{III}\colon X = BF_4)\\(\mathrm{IV}\colon X = PF_6)\end{array}$$

These results are in agreement with recent observations on the reactivity of $[C_5H_5Rh(PMe_3)_2I]I$ towards nucleophiles [10] which also prove that the iodide ligand in cations $[C_5H_5M(PMe_3)_2I]^+$ is quite labile and readily substituted by various nucleophiles.

Complexes III and IV which form light-yellow crystals show a carbonyl band in the infrared spectrum at 2095 cm^{-1}. This suggests according to Angelici's rule [6,11] that the carbonyl carbon atom might be subject to nucleophilic attack. Furthermore, in view of the fact that III and IV are complexes of cobalt(III) and dications, the high CO stretching frequency points to weak π-bonding from the metal to the CO ligand [12] and therefore suggests a weak metal-to-carbon bond. This is confirmed in a number of ways. Thus if $NaBF_4$

is substituted for $AgBF_4$ in the preparation of III, no reaction occurs, indicating that CO alone cannot displace the iodo ligand. Further, if IV is treated with one mol of NaI, the CO ligand is immediately displaced.

$$\mathrm{IV} + \mathrm{NaI} \rightarrow [C_5H_5Co(PMe_3)_2I]PF_6 + CO + NaPF_6 \qquad (3)$$

Whereas III and IV are air stable both in the solid state and in solution they react readily with many solvents at room temperature. Acetone is the only common solvent we have found in which they are both soluble and stable. In dimethyl sulphoxide (DMSO) and dimethyl formamide (DMF), these occurs immediate CO evolution with formation of the stoicheiometric amount of I and decomposition products. In nitromethane, the same reaction occurs, though more slowly. With acetonitrile immediate CO evolution is observed and an orange-red solution is formed, from which the complex $[C_5H_5Co(PMe_3)_2(CH_3CN)](BF_4)_2$ (V) can be isolated as red crystals in good yield.

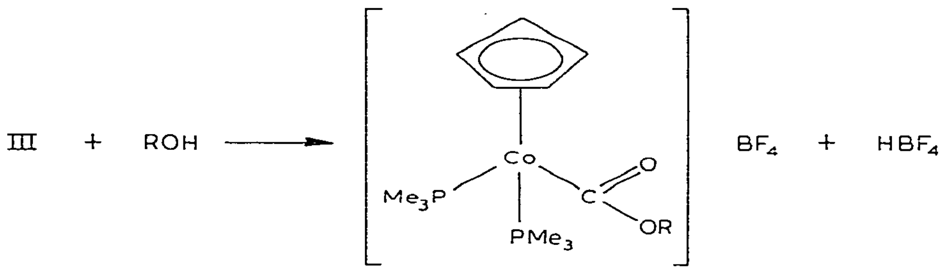
$$[C_5H_5Co(CO)(PMe_3)_2](BF_4)_2 + CH_3CN \rightarrow \underset{(\mathrm{V})}{[C_5H_5Co(PMe_3)_2(CH_3CN)](BF_4)_2} + CO \qquad (4)$$

We attribute the formation of I in other solvents to the instability of complexes of the type $[C_5H_5Co(PMe_3)_2S]X_2$ (S = DMSO, DMF, CH_3NO_2) towards disproportionation.

The infrared spectrum of V in Nujol shows two weak sharp bands at 2290 and 2315 cm^{-1} which we assign to the CH_3CN group, bonded through the nitrogen atom [13]. The presence of two bands could be due to a solid state effect, since the elemental analysis and ^1H NMR spectrum indicate clearly that the compound is not a mixture. The bands are too weak to be seen in the infrared in solution. V is air stable and soluble in solvents such as acetonitrile and nitromethane.

With methanol and ethanol, complex III reacts slowly at room temperature and rapidly at 60°C to give the alkoxycarbonyl complexes VI and VII. They are readily precipitated by ether as yellow powders and form stable solutions in polar organic solvents. The infrared spectra show carbonyl bands at 1626 (VI) and 1632 cm^{-1} (VII). As with other alkoxycarbonylmetal compounds, these frequencies are lower than in their organic analogues, reflecting the superior electron-donating properties of metal centres [6].

At 60°C, complex III is almost completely insoluble in isopropanol and no



(5)

(VI : R = Me)
(VII: R = Et)

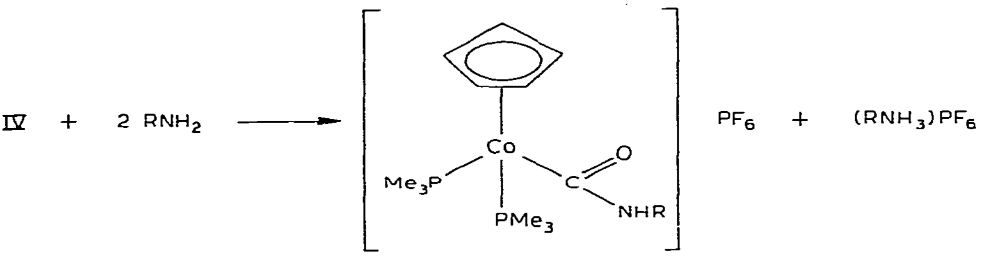
reaction occurred. When III and i-C_3H_7OH were stirred for 24 h at room temperature in acetone, again no reaction occurred. In a subsequent experiment, it was found that EtOH also did not react under these latter conditions. III dissolved in benzyl alcohol on heating at 80°C, but the only products isolated were I and starting material. Alkoxycarbonyl complex formation from III appears therefore to be limited to the simplest alcohols.

In general, alkoxycarbonyl- and carbamoyl-metal complexes have been found to react with excess of a strong acid to regenerate the original carbonyl complex [6]. When complex VI in acetone solution was treated with aqueous 35% HBF_4, there was an immediate reaction and III was isolated in high yield.

$$\mathrm{VI} + \mathrm{HBF_4(excess)} \rightarrow \underset{\text{(III)}}{[\mathrm{C_5H_5Co(CO)(PMe_3)_2}](\mathrm{BF_4})_2} + \mathrm{MeOH} \qquad (6)$$

If complex IV in acetone is treated with an excess of liquid ammonia, a red crystalline compound is obtained which according to the infrared (N—H bands at 3305, 3350 and 3375 cm^{-1}) and ^1H NMR spectra (C_5H_5, 5.24; PMe_3, 1.76 ppm) is $[C_5H_5Co(PMe_3)_2(NH_3)](PF_6)_2$. However, if ammonia is added carefully until the solution just assumes a red-brown colour, addition of ether leads to isolation of the simple carbamoyl complex VIII (eq. 7). The infrared spectrum of the deep-yellow crystalline compound shows N—H bands at 3520 and 3380 cm^{-1}, and bands at 1613 and 1577 cm^{-1} which are attributed to the carbonyl stretching and N—H deformation vibrations, though we cannot say which is which.

Addition of a 10-fold excess of methylamine, ethylamine or benzylamine to IV in acetone leads to the carbamoyl complexes IX—XI as deep-yellow crystals.



(7)

(VIII : R = H)
(IX : R = Me)
(X : R = Et)
(XI : R = CH₂Ph)

IX and X are stable in the reaction mixture for at least 2 h, but XI had to be isolated soon after formation, otherwise only sticky, ill-defined products could be obtained. IX and X show in their infrared spectra N—H bands at 3475 and 3466 cm^{-1}, respectively, and both show a single band at 1595 cm^{-1}, which is presumed to arise from coincidence of the carbonyl stretching and N—H deformation modes. Complex XI shows the N—H stretch at 3470 cm^{-1}, and two bands at 1613 and 1598 cm^{-1}, similar to VIII. All four carbamoyl complexes are soluble in polar organic solvents and the solutions are air-stable. Under the conditions used to prepare VI and IX from III or IV, there was no reaction between VI and methylamine or IX and methanol. Such alkoxycarbonyl-carbamoyl interconversions have been reported in a few cases [6].

Complex X in acetone on treatment with aqueous 35% HBF_4 gave III in high yield, as would be expected from the behaviour of other carbamoyl complexes [6].

$$X + HBF_4(\text{excess}) \rightarrow \underset{\text{(III)}}{[C_5H_5Co(CO)(PMe_3)_2](BF_4)_2} + (EtNH_3)BF_4 \qquad (8)$$

Attempts to obtain complexes analogous to VI, VII and VIII—XI by reactions of III or IV with other nucleophiles failed. Dimethylamine reacted immediately with III in acetone, but no well-defined product could be isolated. With hydrazine hydrate, the expected formation of $[C_5H_5Co(PMe_3)_2NCO]^+$ [6] did not occur and only cobalt(II) species were obtained.

Various experiments to prepare a hydroxycarbonyl complex $[C_5H_5Co(PMe_3)_2$-$COOH]X$ by attack of water either as solvent or in acetone solution, at or above room temperature, gave either no reaction or complex I and decomposition products. The use of base or acid as catalyst was also unsuccessful as was the reaction of III in acetone with H_2O_2. The attempts to hydrolyse the COOMe group in VI with NaOH in water and to effect an "ester-exchange" with NaOEt in ethanol also failed, no reaction occurring in either case. There is in fact only one reported example of a stable hydroxycarbonyl complex [14].

When complex III in acetone was treated with one mol of NaH per mol of III, there was an immediate gas evolution accompanied by formation of I. No reduction products of CO could be detected by gas chromatographic investigations of the reaction mixture. With excess NaH, further decomposition occurred.

^1H NMR spectra

The ^1H NMR spectra of the complexes prepared in this work are summarised in Table 1. In general, the cyclopentadienyl signal appears as a triplet through coupling to the two ^{31}P nuclei. In some cases, the coupling was too small to be observed ($J(PH) < 0.6$ Hz). The trimethylphosphine signal appeared always as a virtual triplet, as has been previously observed with similar compounds [9]. In no case did we observe coupling of the ^{31}P nuclei to the CH_3CN, COOR or CONHR groups. The low solubilities of the complexes together with the broadening due to the nitrogen nucleus prevented observation of the N—H protons of the carbamoyl complexes, but in the spectra of IX—XI this proton manifests itself in coupling to the methyl and methylene groups. It is noticeable that this coupling is considerably smaller in complex X than in IX or XI.

Conclusion

To the best of our knowledge $[C_5H_5Co(CO)(PMe_3)_2]^{2+}$ is the first cationic carbonyl cobalt(III) complex of which stable salts can be isolated, and which is stable in solution. It is a generally accepted rule, that the higher the oxidation state of the metal and the greater the charge on the complex the weaker the

TABLE 1

^{1}H NMR SPECTRA OF COMPLEXES II, IV—XI (δ in ppm, J in Hz; s, singulet; d, doublet; t, triplet; q, quartet)

Complex	Solvent	$\delta(C_5H_5)$	J(PH)	$\delta(PMe_3)$ [a]	δ(MeCN)	δ(COOR)	J(HH)	δ(CONHR) [b]	J(HH)
II	CD_3NO_2	5,28 t	0,7	1,86					
IV	CD_3COCD_3	6,14 t	0,7	2,10					
V	CD_3NO_2	5,50 t	[c]	1,85	2,42				
VI	$(CD_3)_2SO$	5,04 t	0,7	1,49		3,33 s			
VII	$(CD_3)_2SO$	5,00 t	[c]	1,52		3,80 q	6,9		
						1,09 t			
VIII	CD_3COCD_3	5,19 t	1,5	1,63					
IX	CD_3COCD_3	5,15 t	[c]	1,64				2,58 d	4,1
X	CD_3COCD_3	5,08 t	0,7	1,62				3,07 q of d	6,7; 1,3
								0,99 t	6,7
XI	CD_3COCD_3	5,11 t	0,8	1,55				4,08 d	5,2
								6,84 s	

[a] Always as virtual triplet. [b] N—H signal too weak to be observed. [c] $J(PH) < 0,6$ Hz.

metal—carbonyl bond. Only a few examples of cationic carbonylmetal complexes with the metal in the oxidation state +III are as yet known (M = Rh [15,16]; M = Ir [16]). In the case of $[C_5H_5Co(CO)(PMe_3)_2]^{2+}$ the strong donor character of the trimethylphosphine ligands may be important for the stability of the cation as it increases the electron density on the metal thereby strengthening the otherwise weak cobalt(III)—CO bond through increased π-bonding. This strengthening is however insufficient to prevent substitution of CO by such weak ligands as DMF, DMSO, nitromethane or acetonitrile, where in the case of DMF, DMSO and nitromethane an accompanying disproportionation of the primary substitution product occurs with formation of the very stable cation $[C_5H_5Co(PMe_3)_3]^{2+}$ [9].

The marked positive character of the carbonyl-carbon atom caused by weak π-backbonding is demonstrated above all by the ready reaction of the cation $[C_5H_5Co(CO)(PMe_3)_2]^{2+}$ with alcohols, ammonia and amines, and the preparation of further complexes of these types will clearly depend critically on the relative nucleophilicity of the metal and the carbonyl-carbon atoms.

Experimental

Infrared spectra were recorded as Nujol mulls on a Perkin—Elmer 457 and ^{1}H NMR spectra on a Varian T60 using TMS as internal reference.

$C_5H_5Co(CO)I_2$ [7b] and PMe_3 [17] were prepared according to the literature. Solvents were used without further purification. Ammonia and amines were dried over NaOH before use. Elemental analyses (Table 2) were carried out by Miss R. Schedl and Mrs. E. Ullrich of this department and by the Alfred Bernhardt Microanalytical Laboratory.

TABLE 2

ELEMENTAL ANALYSES (found (calcd.) (%)) OF COMPLEXES II, IV—XI

Complex	C	H	N	Co	P	F/I
II	25.09	4.37		10.91	11.46	48.12
	(24.90)	(4.38)		(11.13)	(11.69)	(47.91)
IV	24.65	4.38		9.63	21.06	38.48
	(24.23)	(3.90)		(9.93)	(20.87)	(38.37)
V	31.63	5.46	2.94	11.89	12.45	30.38
	(31.76)	(5.33)	(2.85)	(12.01)	(12.62)	(30.94)
VI	36.15	6.38		13.42	14.78	18.30
	(36.95)	(6.21)		(13.97)	(14.68)	(18.00)
VII	38.28	6.32		13.19	13.95	17.53
	(38.51)	(6.46)		(13.53)	(14.21)	(17.42)
VIII	30.76	5.35	2.83	12.84	19.67	
	(30.95)	(5.42)	(3.01)	(12.68)	(19.99)	
IX	32.59	5.61	2.84	11.89	19.18	23.77
	(32.55)	(5.68)	(2.92)	(12.31)	(19.41)	(23.80)
X	33.78	6.11	2.69	11.70	18.71	22.95
	(34.06)	(5.92)	(2.84)	(11.96)	(18.86)	(23.11)
XI	40.60	6.03	2.44	10.48	16.87	20.70
	(41.07)	(5.62)	(2.52)	(10.63)	(16.75)	(20.53)

Preparation of $[C_5H_5Co(PMe_3)_2I]I$ *(II)*

$C_5H_5Co(CO)I_2$ (4 g, 9.85 mmol)was dissolved in benzene (200 ml) under nitrogen and stirred vigorously. PMe_3 (2 ml, 19.7 mmol) was added and the stirring was continued for 5 min. The yellow-brown precipitate was collected, washed with ether and pentane and dried in vacuo (4.34 g, 83%). The product so obtained contains about 7% of $[C_5H_5Co(PMe_3)_3]I_2$. It was recrystallised from nitromethane by addition of ether. $[C_5H_5Co(PMe_3)_3]I_2$ precipitated out first and was removed, after which addition of excess ether precipitated the product.

Preparation of $[C_5H_5Co(CO)(PMe_3)_2](PF_6)_2$ *(IV)*

Carbon monoxide was passed through acetone (200 ml) and $[C_5H_5Co(PMe_3)_2I]I$ (3 g, 5.05 mmol) was added. As soon as the complex had dissolved, $AgPF_6$ (3.15 g, 12.45 mmol) was added and the mixture stirred for 15 min. The dark brown solution became light yellow and a precipitate formed (AgI). The mixture was filtered and the precipitate was washed with acetone (20 ml). Ether (250 ml) was added to the combined acetone solutions to give the product as a light yellow powder. This was collected, washed with ether and dried in vacuo (3 g, 89%). It can be recrystallised from acetone/ether.

If $AgBF_4$ is used the volume of acetone must be increased about 4-fold, as the BF_4 salt III otherwise precipitates with the AgI.

Preparation of $[C_5H_5Co(PMe_3)_2MeCN](BF_4)_2$ *(V)*

$[C_5H_5Co(CO)(PMe_3)_2](BF_4)_2$ (0.3 g, 0.63 mmol) was stirred for 5 min in acetonitrile (5 ml). Ether (20 ml) was added to the orange-red solution. The resulting precipitate was collected, washed with ether and recrystallised from acetonitrile/ether (0.2 g, 65%).

Preparation of $[C_5H_5Co(PMe_3)_2CO_2Me]BF_4$ *(VI)*

$[C_5H_5Co(CO)(PMe_3)_2](BF_4)_2$ (0.2 g, 0.42 mmol) was stirred in methanol (80 ml) under nitrogen at 60°C for 15 min. The solution was concentrated to 40 ml and ether (600 ml) was added. The yellow precipitate was collected, washed with ether and dried in vacuo (0.15 g, 85%). It can be recrystallised from acetone/ether.

Preparation of $[C_5H_5Co(PMe_3)_2CO_2Et]BF_4$ *(VII)*

$[C_5H_5Co(CO)(PMe_3)_2](BF_4)_2$ (0.1 g, 0.21 mmol) was stirred in ethanol (40 ml) under nitrogen at 60°C for 15 min. The mixture was cooled to room temperature, filtered, and ether (600 ml) was added to the filtrate. The mixture was cooled in ice for 1 h and the resulting yellow precipitate was collected, washed with ether and dried in vacuo (0.06 g, 66%).

Preparation of $[C_5H_5Co(PMe_3)_2CONH_2]PF_6$ *(VIII)*

To $[C_5H_5Co(CO)(PMe_3)_2](PF_6)_2$ (0.3 g, 0.51 mmol) in acetone (18 ml) was added dropwise liquid ammonia until the yellow solution had assumed a reddish tinge. Ether (200 ml) was added and the solution was cooled at —25°C. The resulting deep yellow precipitate was collected, washed with ether and dried in vacuo. It can be recrystallised from acetone/ether (0.2 g, 85%).

Preparation of $[C_5H_5Co(PMe_3)_2CONHMe]PF_6$ *(IX)*

$[C_5H_5Co(CO)(PMe_3)_2](PF_6)_2$ (0.37 g, 0.62 mmol) was stirred under nitrogen in acetone (30 ml) and methylamine (0.25 ml, 6.2 mmol) was added. After 10 min ether (300 ml) was added and the light yellow precipitate was collected, washed with ether and dried in vacuo. It can be recrystallised from methanol/ether (0.26 g, 87%).

Preparation of $[C_5H_5Co(PMe_3)_2CONHEt]PF_6$ *(X)*

$[C_5H_5Co(CO)(PMe_3)_2](PF_6)_2$ (0.2 g, 0.34 mmol) was stirred under nitrogen in acetone (12 ml) and ethylamine (0.22 ml, 3.4 mmol) was added. After 10 min ether (100 ml) was added and the product was treated as above (0.14 g, 84%).

Preparation of $[C_5H_5Co(PMe_3)_2CONHCH_2Ph]PF_6$ *(XI)*

$[C_5H_5Co(CO)(PMe_3)_2](PF_6)_2$ (0.3 g, 0.51 mmol) was stirred under nitrogen in acetone (18 ml) and benzylamine (0.56 ml, 5.1 mmol) was added. After 2 min the reaction mixture was poured into ether (250 ml) and the mixture was cooled at —25°C for 15 min. The supernatant was decanted off and the residue was recrystallised from methanol/ether, the product crystallising as deep yellow almost orange needles on cooling at —25°C (0.12 g, 43%).

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