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Reactions of complexes $Co_2(CO)_6(RC_2R')$ with Group V^0 donor ligands; synthesis and spectroscopic characterization of substituted derivatives $Co_2(CO)_{6-n}(L)_n(RC_2R')$

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Abstract

The reactions of $Co_2(CO)_8$ with asymmetrically substituted alkynes lead to derivatives $Co_2(CO)_6(RC_2R')$ (**1**). Substitution reactions of complexes **1** with PPh_3, $Ph_2P\cdot CH_2CH_2\cdot AsPh_2$ (arphos) and $Ph_2P\cdot CH_2\cdot PPh_2$ (dppm) have been attempted. With PPh_3 monosubstituted chiral tetrahedral molecules, characterized by two differently substituted acetylenic carbon atoms and by two cobalt atoms with different ligand arrangement have been obtained (complexes **2**); some disubstituted derivatives have also been observed (complexes **3**). The equatorial or axial position of the phosphines is discussed. With dppm bridged $Co_2(CO)_4(dppm)\{PhC{\equiv}C\cdot C({=}O)Me\}$ (**5**) is obtained, whereas with arphos a chelate compound (**4**) is the main product. The complexes have been characterized by means of elemental analyses, mass spectrometry and spectroscopic techniques.

Keywords: Cobalt complexes; Carbonyl complexes; Alkyne complexes; Phosphine complexes; Arsine complexes

1. Introduction

The complexes $Co_2(CO)_6(RC{\equiv}CR')$ (**1**) are among the best known organometallic derivatives of cobalt [1] and their reactivity has been extensively studied [2]. Synthetic applications of complexes **1** are of considerable interest in organic chemistry [3].

New applications have also been proposed; these range from protecting or labelling groups in organic and biological reactions [4], to acting as precursors of heterogeneous catalysts supported onto inorganic oxides [5]. Complexes **1** and related derivatives may also act as building blocks or precursors for new materials; reactions with alkynyl- and chloro-alkynyl-phosphines [6a,b], alkynyl- and chloro-alkynyl-sylanes [7a–c] give oligomeric products. The coordination of $Co_2(CO)_6$ units to alkynes has been used to obtain oligomeric precursors of metal-doped polyacetylenes [8] or to link other metal fragments [9].

Chiral complexes **1** might be of considerable interest as starting materials for many of the above applications. The easy synthesis of complexes **1** allows the study of their substitutional reactivity with Group V^0 donor ligands, aimed at obtaining high yields of chiral complexes presumably stable to racemization in solution. In this paper we report on the reactions of some recently characterized complexes **1** [10] with phosphines and diphosphines; the products are monosubstituted or disubstituted chelate or bridged complexes and have been characterized by spectroscopic techniques and in particular by multinuclear NMR.

2. Experimental

2.1. General experimental details. Materials. Analysis of the products

$Co_2(CO)_8$ (Strem Chemicals), PPh_3 (Aldrich), bisdiphenylphosphino methane (dppm), 1-diphenylphosphino-2-diphenylarsino ethane (arphos) (Strem Chemicals), and the alkynes were commercial products (Ald-

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$R=H$; $R'=C(Me)Ph(OH)$, $CMe_2NHCOC_6H_9$; $L=PPh_3$; $n=1$, 2.
$R=Ph$; $R'=Me$; $L=PPh_3$; $n=1$, 2.
$R=Ph$; $R'=C({=}O)Me$; $L=PPh_3$, dppm, arphos; $n=1$, 2.

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rich, Janssen, Fluka) and were used as received. *N*-(α,α-Dimethylpropargyl)-1-cyclohexencarboxamide was obtained by established procedures [11].

Unless otherwise specified all reactions were performed in conventional three-necked flasks equipped with gas inlet, reflux condenser and mercury check valve; distilled dry toluene was used as a solvent under a dry N_2 atmosphere. The reaction mixtures were filtered under N_2 and brought to small volume under reduced pressure; these were purified by means of TLC preparative plates (Kieselgel P.F. Merck, eluants mixtures of light petroleum 40–70 °C and diethyl ether). The products collected were crystallized, when possible, from heptane, heptane–$CHCl_3$ or heptane–toluene mixtures kept at low temperature under nitrogen.

The elemental analyses were performed on an F&M C,H,N analyzer; the cobalt and phosphorus analyses were obtained from F. Pascher Laboratories (Remagen, Germany). IR spectra were measured on a Perkin-Elmer 580 B instrument. The ^1H, ^{31}P and $^{13}C\{^1H\}$ NMR spectra were registered on JEOL JNM 270 FT and EX-400, or Brucker CPX 200 FT instruments; the spectra were obtained in $CDCl_3$ solutions, at room temperature, with external TMS or H_3PO_4 as standards. The FAB mass spectra were registered on a Kratos MS-80 instrument in a nitrobenzyl alcohol matrix.

2.2. Reactions of complexes 1 with Group V^0 donor ligands

2.2.1. Reactions with PPh$_3$

Reflux of 1.0 g (2.31 mmol) of $Co_2(CO)_6\{HC_2C(Me)Ph(OH)\}$ (**1a**) with 0.75 g (2.86 mmol) of PPh_3 for 2 min yields a dark brown solution. TLC purification indicates the presence of parent **1a** (5%), red–brown $Co_2(CO)_5(PPh_3)\{HC_2C(Me)Ph(OH)\}$ (**2a**, 50%), brown–purple $Co_2(CO)_4(PPh_3)_2\{HC_2C(Me)Ph(OH)\}$ (**3a**, 10%) and considerable decomposition (15%).

*Complex **2a***: $Co_2C_{33}H_{25}O_6P$, MW 666.4. *Anal.* Found: Co, 17.2; C, 60.8; H, 3.8; P, 4.7. Calc.: Co, 17.69; C, 59.48; H, 3.78; P. 4.65%. IR (ν(CO), C_7H_{16}): 2068vs, 2024vs, 2006vs, 1997m (b) cm^{-1}. ^1H NMR: 7.56–7.18mm (Ph); 5.47d, 5.45d, (HC≡); 1.79s (OH), 1.32s (CH_3). ^{13}C NMR: 15.1s, 22.5s (CH_3); 65.7s, ($C\cdot CH_3$); 104.0d (C_{alkyne}); 124.4–133.2mm (Ph); 149.0d (C_{alkyne}); 200.1m (b), 205.2m (b) (CO). ^{31}P NMR: +49.26s (int. 100); +48.05s (58). FAB mass spectrum: 666 *m/z*, loss of carbonyls, followed by complex fragmentation.

*Complex **3a***: $Co_2C_{50}H_{40}O_5P_2$, MW 900.7. *Anal.* Found: Co, 13.6; C, 65.8; H, 4.9; P, 7.2. Calc.: Co, 13.09; C, 66.68; H, 4.48; P. 6.88%. IR: 2028vs, 1988s (sh), 1976vs cm^{-1}. ^1H NMR: 7.64–6.99mm (Ph); 6.62d (HC≡); 1.70s (OH); 1.18s (CH_3). ^{31}P NMR: +47.8s (100); +46.2s (93). FAB mass spectrum: 872 *m/z* ($P^+ - CO$) and complex fragmentation.

A suspension of $Co_2(CO)_6[HC_2\cdot CMe_2NHCO(C_6H_9)]$ (**1b**) and a 2:1 excess of PPh_3 was warmed in toluene for 11 min till incipient reflux. The colour turned to dark brown and after TLC purification traces of **1b**, dark red **2b** (35%) and purple **3b** (35%) were collected; small amounts of decomposition products were also observed.

*Complex **2b***: $Co_2C_{35}H_{32}O_6NP$, MW 711.4. *Anal.* Found: C, 59.4; H, 4.7; P, 4.2. Calc.: C, 59.08; H, 4.53; P, 4.35%. IR (C_7H_{16}): 2068vs, 2021vs, 2002vs (vb), 1966s (b), 1685m cm^{-1}. ^1H NMR: broad signals at 7.30 (HC≡), 6.70, 6.24, 5.75 (C_6H_9), 2.20 (N–H), 1.67 (CH_3). ^{31}P NMR: +47.3s. ^{13}C NMR: 14.1s, 21.6s, 22.3s, 24.3s, 25.5s, 30.1s, 31.6s (CH_3, C_6H_9); 56.6s, 74.5s (CH/CH_2, C_6H_9); 103.6s ($C{\equiv}\mathit{C}{-}C$); 128.4–133.2mm (Ph/CH, C_6H_9); 167.3s ($H{-}C{\equiv}\mathit{C}$); 201.1s (b) (3 CO), 205.4s (b) (2 CO).

*Complex **3b***: $Co_2C_{52}H_{47}O_5P_2N$, MW 945.8. *Anal.* Found: Co, 12.5; C, 66.8; H, 5.2. Calc.: Co, 12.46; C, 66.04; H, 5.01. IR (ν(CO), C_7H_{16}): 2020vs, 1996s, 1968m, 1946m (b) cm^{-1}. ^{31}P NMR: +20.96s. FAB mass spectrum: 945 *m/z* (low intensity) and complex fragmentation.

A suspension of $Co_2(CO)_6[PhC_2\cdot C(=O)Me]$ (**1c**) and a 2:1 excess of PPh_3 was refluxed in toluene for 2 min, till the colour turned dark brown. After TLC purification, traces of **1c**, red–brown **2c** (40%) and purple **3c** (40%) were collected: very small decomposition occurred.

*Complex **2c***: $Co_2C_{33}H_{23}O_6P$, MW 664.4. *Anal.* Found: C, 60.3; H, 3.9; P, 4.4. Calc.: C, 59.66; H, 3.49; P, 4.66%. IR (C_7H_{16}): 2070vs, 2025vs, 2012vs, 1977m (b), 1721w cm^{-1}. ^1H NMR: 7.47m, 7.20mm (Ph), 2.60s (Me). ^{31}P NMR: +45.2s. ^{13}C NMR: 32.5s, 33.3s (CH_3, CH_2); 128.3–131.1mm (Ph); 138.8d (C≡C); 205.7s (–(C=O)–); 206.6s (2 CO); 206.8s (b) (3 CO).

*Complex **3c***: $Co_2C_{50}H_{38}O_5P_2$, MW 898.7. *Anal.* Found: C, 67.0; H, 4.5; P, 6.6. Calc.: C, 66.83; H, 4.26; P, 6.89%. IR (C_7H_{16}): 2027vs, 1986s (sh), 1978vs, 1730vw cm^{-1}. ^{31}P NMR: +42.97s.

Treatment of 1.0 g (2.49 mmol) of $Co_2(CO)_6(PhC_2Me)$ (**1d**) with 1 g (3.81 mmol) of PPh_3 in toluene, under CO_2, for 3 min reflux gives a dark brown suspension; TLC purification shows the presence of unreacted parent **1d** (25%), brown $Co_2(CO)_3(PPh_3)(PhC_2Me)$ (**2d**, 55%), purple $Co_2(CO)_4(PPh_3)_2(PhC_2Me)$ (**3d**, 15%) and a small amount of decomposition.

*Complex **2d***: $Co_2C_{32}H_{23}O_5P$, MW 636.4. *Anal.* Found: C, 60.5; H, 3.7; P, 4.9. Calc.: C, 60.40; H, 3.64; P, 4.87%. IR (ν(CO), C_7H_{16}): 2069vs, 2025vs, 2009vs, 1992m (b) cm^{-1}. ^1H NMR: 7.39m (b) (20H, Ph); 2.41s (b) (3H, CH_3). ^{13}C NMR: 20.3s (CH_3); 86.2s, 87.9s (C_{alkyne}); 126.2–134.2m (Ph); 139.6s (C_{alkyne}); 201.6b, 205.4b, CO. ^{31}P NMR: +51.67s.

Complex 3d: $Co_2C_{49}H_{38}O_4P_2$, MW 870.6. *Anal.* Found: C, 68.0; H, 4.5; P, 7.2. Calc.: C, 67.60; H, 4.40; P, 7.11%. IR (ν(CO), C_7H_{16}): 2030vs, 1984s, 1970vs cm^{-1}. ^1H NMR: 7.37s, 7.21d, 6.96s, 6.86s (35H, Ph); 1.60s (3H, CH_3). ^{13}C NMR: 18.9s (CH_3); 80.4s, 82.2s (C_{alkyne}); 124.8–135.1m (Ph); 140.7s (C_{alkyne}); 207.0vb, CO. ^{31}P NMR: +50.96s.

2.2.2. *Reactions of 1c with arphos and dppm*

Complex **1c** was reacted with a 1.5 molar excess of arphos in toluene; after 3 min reflux the dark brown solution contained about 40% of parent **1c**, 40% of dark brown $Co_2(CO)_4$(arphos){$PhC_2C(=O)Me$} (**4c**), and considerable decomposition.

Complex 4c: $Co_2C_{40}H_{32}O_5PAs$, MW 816.4. *Anal.* Found: C, 58.7; Co, 14.8; H, 4.1; P, 3.7. Calc.: C, 58.84; Co, 14.44; H, 3.95; P, 3.79%. IR (C_7H_{16}): 2070s, 2036vs, 2025(sh), 2008vs, 1998s, 1727w cm^{-1}. ^1H NMR: 7.52m, 7.25mm (Ph), 2.50s (Me), 1.20m, 0.80m (CH_2, arphos). ^{31}P NMR: +30.42s. ^{13}C NMR: 23.4s, 29.7d, 31.4s (CH_3); 77.1s, 77.7s (CH_2, arphos); 85.0s, 94.0s ($C\equiv C$); 127.2–134.3mm (Ph, arphos); 142.4s ($C\equiv C$); 203.2s (b) (3 CO); 206.4s (b) (1 CO); 207.0s ($-C(=O)-$). FAB mass spectrum: $P^+ = 816$ m/z, loss of four carbonyls, in competition with a complex fragmentation involving loss of phenyl, methyl and further carbonyl from {$-C(=O)Me$}.

Complex **1c** was reacted with a twofold molar excess of dppm in refluxing toluene for 2 min; TLC of the dark purple solution showed the presence of about 40% parent **1c**, purple $Co_2(CO)_4$(dppm){$PhC\equiv C\cdot C(=O)Me$} (**5c**, 40%) and decomposition.

Complex 5c: $Co_2C_{39}H_{30}O_5P_2$, MW 758.5. *Anal.* Found: C, 61.3; H, 4.2; P, 8.4. Calc.: C, 61.76; H, 3.99; P, 8.17%. IR (C_7H_{16}): 2035s, 2012vs, 1989s, 1722w cm^{-1}. ^1H NMR: 7.48–7.30mm (Ph); 2.28m, 2.60m (CH_2, dppm); 1.20s (CH_3). ^{31}P NMR: +32.27s. ^{13}C NMR: 13.9s, 22.5s, 30.6s, 31.4s, 34.6m (CH_3, CH_2, dppm); 126.3–133.0mm (Ph, dppm); 138.1m ($C\equiv C$); 141.9s ($C\equiv C$); 201.2s (b) (2 CO); 206.7d (b) ($-C(=O)-$ and 2 CO). FAB mass spectrum: $P^+ = 758$ m/z, loss of four CO, in competition with complex fragmentation.

3. Results and discussion

3.1. *Some comments on complexes 1*

As previously discussed [10] the reactions of $Co_2(CO)_8$ with asymmetrically substituted alkynes lead to high yields of complexes **1**. These complexes show CO ligands falling into two sets; axial (2 CO) and equatorial (4 CO), respectively; if the alkynes bear substituents R=/=R′ as in the present case, the eq and eq′ CO become inequivalent (Fig. 1). This has been shown experimentally [12].

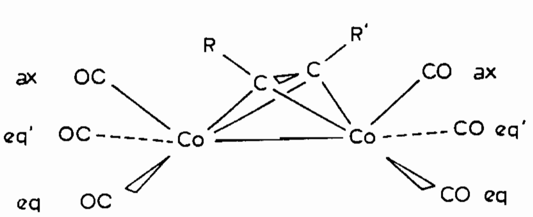

Fig. 1. Inequivalent sets of carbonyls in complexes 1.

3.2. *Synthesis of complexes 2–5*

The reactions of complexes **1** with Group V^0 donor ligands occur smoothly and give good yields of the monosubstituted derivatives **2**, and lower yields of the disubstituted complexes **3**; in particular, complex **2d** can be obtained with considerably high overall yields. Only one isomer for each complex **2** has been obtained, with the exception of **2a** which apparently is formed in two isomers when judging by the spectroscopic results; this could be due either to axial–equatorial substitution or to the formation of optical isomers.

The reactions of **1c** with arphos and dppm lead to high yields of complexes **4c** and **5c**, respectively. In similar conditions, $Co_2(CO)_6(HC_2Ph)$ reacted with arphos giving a unseparable mixture of bridged and chelate isomers [13].

Complexes $Co_2(CO)_6L_n$ (L = Group V^0 donor; $n=1$, 2) are well established catalysts for hydroformylation and silylformylation reactions [14]. The reactions of these derivatives with alkynes could lead to complexes **3**; however, this synthetic approach cannot be followed, at least for PPh_2H or P_2Ph_4. The alkynes insert into metal–phosphorus bonds giving more complex structures [15]. The direct reaction of $Co_2(CO)_8$ with alkynes followed by substitution with phosphines or bidentate ligands gives high yields of the chiral products with unmodified alkyne substituents.

3.3. *Spectroscopic characterization of complexes 2–5*

The IR and NMR spectra of complexes **2** indicate the presence of unaltered alkynes and the ^{31}P NMR shows the presence of phosphorus; the ^{31}P chemical shifts fall in the common range for coordinated phosphorus atoms. The elemental analyses are consistent with the formulation as monosubstituted derivatives $Co_2(CO)_5(PPh_3)(RC_2R')$. Complexes **3** were identified on the basis of their analytical data and, for **3a**, of a mass spectrum; the broad ^{13}C NMR signals for the

CO do not make it clear whether both the phosphines are equatorial or not. The presence of unmodified alkynes is evidenced by ^{1}H NMR.

In complexes **4c** and **5c** (found in only one isomer each) IR and ^{1}H NMR still indicate the presence of intact alkynes and ^{31}P NMR that of phosphorus-containing ligands; for the arphos derivative **4c** ^{31}P NMR did not allow a unequivocal structural hypothesis; the IR spectrum of the complex is similar to those of the monosubstituted complexes **2**. ^{13}C NMR and the elemental analysis however accord with a chelate disubstituted complex. The possibility of the formation of a $\{Co_2(CO)_5(alkyne)\}_2$(arphos) dimer [16] is ruled out by the FAB mass spectrum of the complex which confirms the formulation as a chelate derivative with four (terminal) carbonyls.

^{31}P NMR of **5c**, which also shows an IR spectrum different from **4c** and comparable with that of **3c**, indicates that the ligand is symmetrically bound; evidence for bridging on two metals is given by the presence of two sets of 2 CO ligands in 2:2 intensity in the ^{13}C NMR.

The different coordinating behaviours of dppm and arphos have been previously reported and discussed for ruthenium acetylide clusters [17].

A comparison of the ^{13}C NMR spectra of **1b**, **1c** and of the substituted derivatives **2** and **3** shows well related signals for the coordinated organic moieties; however, complexes **1** show a single broad resonance for the six carbonyls at room temperature, indicative of fluxionality. By contrast, complexes **2** show two distinct resonances, indicating the presence of two different carbonyl sets, each on a different metal atom. Finally, complexes **4** and **5** show, as already discussed, two sets of slightly inequivalent carbonyls with 2:2 or 1:3 integrated intensities for **5c** and **4c**, respectively.

The structures proposed for complexes **2**–**5** are given in Fig. 2.

On the basis of the available spectroscopic data only, we cannot state whether the Group V^0 donor ligands are in an axial or equatorial position; however, some hypotheses can be advanced on the basis of indirect evidence. In complexes **2** the phosphine is expected to substitute an axial CO as found in closely related complexes [18–20][1]; a possible exception could be represented by the two isomers of **2a**. In complex **5c** the ligand is expected to be eq–eq or eq′–eq′ as found for $Co_2(CO)_4(\mu\text{-dppm})[\mu\text{-}C_2(CH_2SMe)_2]Mo(CO)_4$ [22*]. For **4c** the more likely disposition should be eq–eq′ on the same cobalt atom; this would give rise to two isomers (ax/eq, ax/eq′). An interesting consequence of such a situation is that not only the CoC_2 moiety, but also the substituted cobalt atom, becomes chiral.

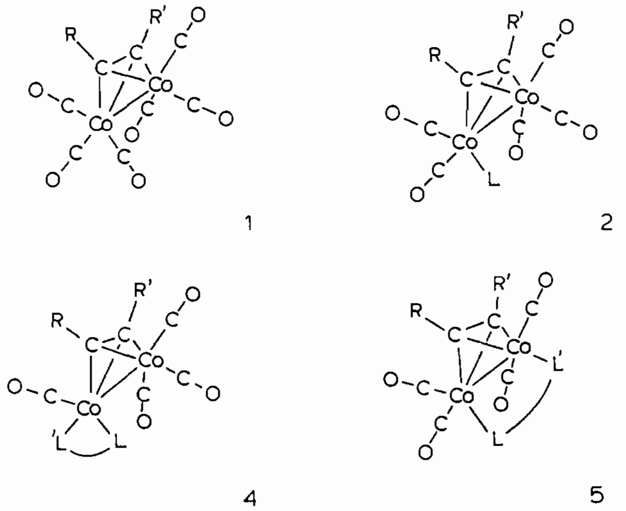

Fig. 2. Structure of complexes **1** and proposed structures of complexes **2**, **4** and **5**.

Several phosphine-substituted $Co_2(CO)_{6-n}(RC{\equiv}CR')(L)_n$ complexes have been reported for R = R′ [6–8,21] and for R =/= R′ [18–20,23] the latter being chiral. By contrast a few examples of dppm-containing derivatives are known [23] and, to our knowledge, complex **4c** represents the first example of an arphos derivative.

A variety of different approaches leading to chiral cobalt complexes has been proposed [24]. In addition to making the chiral complexes **2** by substitution of carbonyls with Group V^0 donor ligands, there are several other possibilities, namely: (i) the use of heterobimetallic M–M′ frames [25] and, more interestingly (ii) the possibility of obtaining diastereoisomers with $Co_2(CO)_5(PPh_3)$ frames and acetylenes with substituents bearing chiral carbon atoms [24a,26, see also 3j,k,l, and 4] or (iii) coordination of RC_2R' alkynes on $Co_2(CO)_5(PR_3)$ frames [20]. Finally, one cobalt atom may become chiral when substituted with arphos as discussed above. Examples of clusters with chiral (racemic) propargyl alcohols as substituents and a phosphine ligand are given by the complexes $Co_2(CO)_5(PPh_3)(R^1C_2{\cdot}CH(OH)R^2)$ (R^1 = H, R^2 = Me, Ph, Bu^t; R^1 = Ph, R^2 = Me, Pr^i); these can be obtained with diastereoisomeric excess ranging from 10 to 95% and can be separated by flash chromatography on silica [27]. It is worth noting that the derivatives exhibit significant configurational stability and isomerize only after days at room temperature. The relative stereochemistry of the major isomer with R^1 = H, R^2 = Ph has been established by X-ray diffraction [27].

Separation techniques for enantiomeric complexes **1** are under development: the use of cyclodextrines has been shown possible [28], but direct phase HPLC on chiral columns [29] seems to give the best results.

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[1] Complex $Co_2(CO)_5(PPh_3)[HC{\equiv}CH(OH)Ph]$ with a chiral carbon is obtained in two diastereoisomers in different yields, which were separated by chromatography [19]. Complex $Co_2(CO)_5(PR_3)(HC{\equiv}CPh)$ contains a chiral phosphorus atom [20].

We have attempted without any success TLC separations of the isomers of complex **2a** and of the mixture of complexes obtained from $Co_2(CO)_6(HC_2Ph)$ by using high performance TLC pre-coated plates CHIR (Merck) and a wide variety of eluants or eluant mixtures. HPLC/CI experiments are in progress.

4. Conclusions

The reactions described in this paper represent a general and convenient way to obtain chiral organometallic molecules of considerable synthetic and catalytic interest in a two-step process with acceptable overall yields and starting from easily available materials. Unfortunately we could not find, at least at present, easily available and convenient methods for the separation of the optical isomers, which is one of the key steps for the use of the above clusters as precursors of new organic and organometallic molecules of interest either in synthetic organic chemistry or in material chemistry.

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