Replacement of [RuH₂(PMe₃)₄] by [RuH₂(PEt₃)₄] switches reaction products: synthesis of fluoride-bridged diruthenium complexes

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The fluoride-bridged ruthenium dimers $[Ru_2(\mu\text{-}F)_3(PR_3)_6][F(HF)_n]$ (R = Et, Pr, Bu; $n \approx 3$) were synthesised by the reactions of the cis-$[RuH_2(PR_3)_4]$ complexes with $NEt_3 \cdot 3HF$ in THF; the crystal structure of $[Ru_2(\mu\text{-}F)_3(PEt_3)_6]OTf$, formed by subsequent reaction with NH_4OTf, reveals Ru–F distances in the range 2.132(2)–2.170(2) Å and Ru–F–Ru angles in the range 91.72(7)–93.02(7)°.

Introduction

Interest in fluorine as a ligand in coordination chemistry is flourishing because of its potential for fluorination reactions, its unusual reactivity and its catalytic activity.[1,2] While some argue that fluorine acts as an exceptionally strong π-donor,[3,4] Mezzetti and Becker have suggested that it is the ionic character of the metal–fluorine bond that is the dominant characteristic.[5] They note that most fluoro complexes of late transition metals are stabilised through push–pull effects through π-acceptor ligands. If such stabilisation is absent, they argue that fluoro complexes are labile and very reactive towards nucleophilic attack. Their conclusions are supported by re-analysis by Tilset *et al.* of their data on the electrochemistry of half-sandwich iron complexes.[1] The interpretation of π-donor effects usually relies on CO-stretching frequencies for guidance, but their validity as indicators has been questioned.[6]

Methods of introduction of fluorine have been surveyed in recent reviews,[3,7] but there is little systematic understanding of how to select fluorination reagents. Recently, Togni and co-workers reported the synthesis of $[RuF(dppp)_2]PF_6$, and cis-$[RuF_2(dppp)_2]$ complexes with TlF and Me_4NF as fluorine sources.[1,8] Other recent examples of fluoride in combination with soft ligands at group 8, 9 and 10 metals include the Ir(III) hydride fluoride $[Ir(H)_2F(P^tBu_2Ph)_2]$ complex synthesised with Me_4NF,[9] $[(\eta^5\text{-}C_5Me_5)Ir(Ph)(F)(PMe_3)]$ made with $[(Me_2N)_3S]^+$-$(Me_3SiF_2)^-$,[10] $[(\eta^5\text{-}C_5H_5)Ru(F)(CO)(PCy_3)]$ and $[Ir(Cl)(F)_2(PEt_3)_2(CO)]$ *via* XeF_2,[11,12] trans-$[RhF(P^iPr_3)_2(PhCCH)]$ *via* reaction with Bu_4NF,[13] and trans-$[Pd(Ph)(F)(PPh_3)_2]$ by reaction with AgF or $NEt_3 \cdot 3HF$.[4,14] The fluorine-bridged cation $[Ru_2(\mu\text{-}F)_3(CO)_2(PPh_3)_4]^+$ was made by reaction of metal hydride complexes with anhydrous HF.[15]

We have introduced fluorine at a metal centre by C–F bond activation (*e.g.* in trans-$[Ni(C_6F_5)(F)(PEt_3)_2]$)[16] and by reaction with $NEt_3 \cdot 3HF$ (*e.g.* trans-$[Ru(H)(FHF)(dmpe)_2]$,[17] trans-$[Pt(H)(FHF)(PCy_3)_2]$).[18] Whittlesey and coworkers have used C–F activation at fluorinated alkenes to form trans-$[Ru(F)(FHF)(dmpe)_2]$ in a related process.[19] Both C–F activation and $NEt_3 \cdot 3HF$ allow reaction in standard glassware. Until now, use of $NEt_3 \cdot 3HF$ with ruthenium and platinum phosphine complexes has resulted in formation of bifluoride ligands in which a hydrogen bond is formed between the metal fluoride and HF.

The characteristic features of the low-temperature NMR spectra of the bifluoride complexes include ^{19}F resonances at δ *ca.* −300 for the proximal fluorine and δ *ca.* −165 for the distal fluorine. The acidic protons resonate at δ *ca.* 13. The value of $J(HF)$ for the distal fluorine lies in the range 300–400 Hz. All

the complexes exhibit dynamic exchange processes necessitating the use of low-temperature NMR spectroscopy. The F ⋯ F separation is considerably less than twice the van der Waals radius of fluorine (1.4 Å).[20]

Most of the complexes described above contain fluorine as a terminal ligand, but it is also well established as a double and triple bridging ligand. Cyclic complexes containing bridging fluorine have been thoroughly reviewed by Roesky and Haiduc.[21] Of these, a small set contain phosphines as co-ligands. Important examples are $[\{M(CO)_2L_2\}_2(\mu\text{-}F)_3]^-$ (M = Mo, W), $[\{MoH_2L_3\}_2(\mu\text{-}F)_3]^+$ and $[\{M(CO)L_2\}_2(\mu\text{-}F)_3]^+$ (M = Ru, Os), where L = tertiary phosphine.[15,22,23]

Reaction of cis-$[RuH_2(diphos)_2]$ (diphos = dmpe, depe, dppe, dppp) with polyfluorinated benzenes or $NEt_3 \cdot 3HF$ produces the bifluoride complexes, trans-$[Ru(H)(FHF)(diphos)_2]$.[17,24] In contrast, cis-$[RuH_2(PMe_3)_4]$ reacts with $NEt_3 \cdot 3HF$ to form cis-$[Ru(FHF)_2(PMe_3)_4]$.[24] In this paper, we show that the corresponding reaction of cis-$[RuH_2(PR_3)_4]$ (R = Et, Pr, Bu) takes a different course from that of cis-$[RuH_2(PMe_3)_4]$ or cis-$[RuH_2(diphos)_2]$ and yields dinuclear ruthenium complexes with fluoride bridges, opening up new applications of this reagent and a new route to fluoride complexes with phosphine as ancillary ligands.

Results

The hydride complexes cis-$[RuH_2(PR_3)_4]$ (R = Et, Pr and Bu) were reacted with $NEt_3 \cdot 3HF$ in THF solution to give dihydrogen and a group of complexes identified below as $[Ru_2(\mu\text{-}F)_3(PR_3)_6][F(HF)_n]$ (n = 1–5). A stoichiometry such as in eqn. (1) is appropriate.

The complexes analyse satisfactorily for the presence of the bifluoride anion, *i.e.* n = 1, but the ^1H NMR integrations indicate an average composition of $n \approx 3$. The discrepancy may be explained if the complexes undergo loss of HF prior to combustion. The anion in the salts undergoes exchange with PF_6^-, OTf^- or halide, when treated with KPF_6, NH_4OTf and KX (X = Cl, Br, I) in THF. The chloride salt is formed overnight on dissolving the salts in $CHCl_3$ or CH_2Cl_2. The polyfluoride salts are stable in solution under argon and in the solid state. The other salts are air-stable.

The principal NMR data are listed in Table 1. On formation of $[Ru_2(\mu\text{-}F)_3(PEt_3)_6][F(HF)_n]$, a broad resonance appears in the ^1H NMR spectrum at room temperature at δ 11.5 assigned to the $[F(HF)_n]^-$ protons. On cooling this resonance starts to separate and split into a broad doublet at 173 K ($J(HF)$ = 339 Hz).
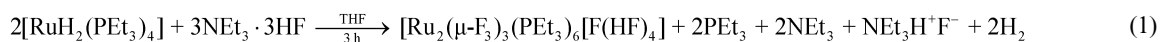
$$2[RuH_2(PEt_3)_4] + 3NEt_3 \cdot 3HF \xrightarrow[3\,h]{THF} [Ru_2(\mu\text{-}F_3)(PEt_3)_6[F(HF)_4] + 2PEt_3 + 2NEt_3 + NEt_3H^+F^- + 2H_2 \qquad (1)$$

Table 1 Selected NMR data (CD$_2$Cl$_2$) recorded at 300 K for [Ru$_2$(μ-F)$_3$(PR$_3$)$_6$][F(HF)$_n$]

	δ ^{1}H (FHF)	δ ^{31}P{^{1}H}	δ ^{19}F (μ-F)	δ ^{19}F (FHF)
[Ru$_2$(μ-F)$_3$(PEt$_3$)$_6$][F(HF)$_n$]	11.5	45.5 m	−352.5	−176.2
[Ru$_2$(μ-F)$_3$(PPr$_3$)$_6$][F(HF)$_n$]	11.7	42.7 m	−346.0	−170.5
[Ru$_2$(μ-F)$_3$(PBu$_3$)$_6$][F(HF)$_n$]	11.7	42.2 m	−354.5	−171.0

The ^{31}P{^{1}H} NMR spectrum of each complex shows a temperature independent second-order pattern with a sharp doublet at the outside and an inner broad unresolved doublet (Fig. 1(a)) similar to that observed for [{MoH$_2$(PMePh$_2$)$_3$}$_2$(μ-F)$_3$]$^+$.[23] The ^{19}F NMR spectra of the [Ru$_2$(μ-F)$_3$(PR$_3$)$_6$][F(HF)$_n$] complexes shows two resonances, one at δ *ca.* −170 and one at δ *ca.* −350. The low field resonance is broad at room temperature but resolves into a doublet of multiplets on cooling (J(HF) *ca.* 340 Hz). The second ^{19}F resonance is a multiplet (Fig. 1(b)) that collapses to a singlet with phosphorus decoupling; this resonance broadens at low temperature.
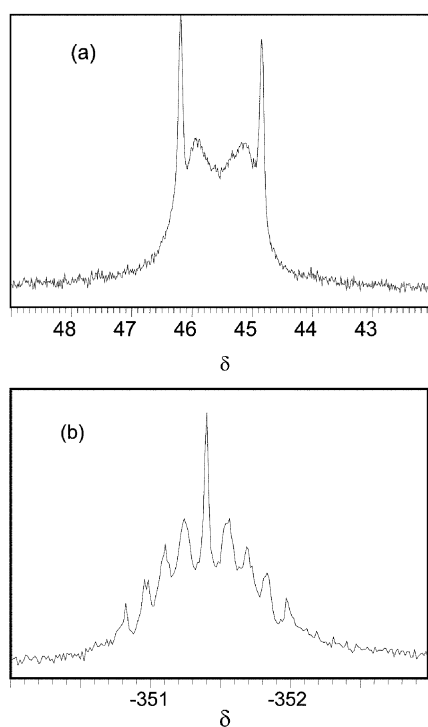
Fig. 1 NMR spectra for [Ru$_2$(μ-F)$_3$(PEt$_3$)$_6$][F(HF)$_n$] in [^{2}H$_2$]dichloromethane at room temperature (a) ^{31}P spectra (121.49 MHz), (b) ^{19}F spectra (282.404 MHz).

Replacement of the [F(HF)$_n$]$^-$ ion by hexafluorophosphate, triflate and chloride on salt metathesis is confirmed by NMR spectroscopy. The ^{1}H NMR spectra show that the broad resonance at δ 11.5 of the [F(HF)$_n$]$^-$ has disappeared, but there was no change in the phosphine resonance in the ^{31}P NMR spectra. In the ^{19}F NMR spectrum, the broad resonance at δ −170 disappeared while the fluorine resonance at δ *ca.* −350 still remained. If these results are compared with the behaviour of mononuclear Pt and Ru bifluoride complexes on reaction with chloride,[18,24] we find that *both* the proximal and distal fluorine resonances disappeared for the bifluoride complexes on chlorination.

The [(R$_3$P)$_3$Ru(μ-F)$_3$Ru(PR$_3$)$_3$]$^+$ ion forms a second-order spin system A^{1}A^{2}A^{3}X$'$X$''$X$'''$A^{4}A^{5}A^6 where A^n designates magnetically inequivalent phosphorus nuclei. The resulting ^{31}P NMR spectrum resembles that of an {AX$_n$}$_2$ spin system, but the ^{19}F resonance simplifies to resemble a binomial multiplet. We have shown that the [F(HF)$_n$]$^-$ ion in the ruthenium salts formed initially could be replaced with negligible change in the NMR spectrum of the cation. The NMR characteristics of

Table 2 Selected bond lengths (Å) and angles (°) for [Ru$_2$(μ-F)$_3$-(PEt$_3$)$_6$](OTf)·0.5THF

Ru(1) ⋯ Ru(2)	3.1081(4)	Ru(1)–P(1)	2.2585(9)
Ru(1)–F(1)	2.1607(18)	Ru(1)–P(2)	2.2883(9)
Ru(2)–F(1)	2.1702(19)	Ru(1)–P(3)	2.2644(9)
Ru(1)–F(2)	2.1315(18)	Ru(2)–P(4)	2.2657(9)
Ru(2)–F(2)	2.1526(18)	Ru(2)–P(5)	2.2626(9)
Ru(1)–F(3)	2.1526(18)	Ru(2)–P(6)	2.2729(9)
Ru(2)–F(3)	2.1415(18)		
Ru(1)–F(1)–Ru(2)	91.72(7)	F(2)–Ru(1)–F(3)	74.46(7)
Ru(1)–F(2)–Ru(2)	93.02(7)	F(2)–Ru(1)–F(1)	73.61(7)
Ru(1)–F(3)–Ru(2)	92.74(7)	F(3)–Ru(1)–F(1)	73.03(7)
F(2)–Ru(1)–Ru(2)	43.76(5)	F(2)–Ru(1)–P(1)	165.12(5)
F(3)–Ru(1)–Ru(2)	43.49(5)	F(3)–Ru(1)–P(1)	92.50(5)
F(1)–Ru(1)–Ru(2)	44.26(5)	F(1)–Ru(1)–P(1)	95.99(5)
P(1)–Ru(1)–P(2)	98.88(3)	P(1)–Ru(1)–P(3)	94.42(3)
P(3)–Ru(1)–P(2)	94.23(3)		

the [F(HF)$_n$]$^-$ salt of this binuclear fluoride cation are, however, confusingly similar to those of a bifluoride complex in which one fluorine is bound directly to the metal. Nevertheless, the salt metathesis reactions provide a clear distinction between the bound bifluoride complex and the salts of [F(HF)$_n$]$^-$.

The IR spectra (Nujol mull) showed ν(MH) bands for the dihydride starting material at 1800–1900 cm^{-1} that disappeared on reaction with NEt$_3$·3HF yielding two new broad product bands at 1733 cm^{-1} and 2682 cm^{-1} (R = PEt$_3$). These bands are absent from the IR spectra of the hexafluorophosphate, triflate and chloride salts. They are assigned to ν(HF) of the [F(HF)$_n$]$^-$ ion; their frequencies are close to those found in simple bifluoride salts.[25] Anions of this type have been described previously with n = 2–7.[26]

Yellow crystals of [Ru$_2$(μ-F)$_3$(PEt$_3$)$_6$][F(HF)$_n$] formed overnight from a saturated THF solution of the compound at −25 °C under argon, but the anions proved to be disordered and could not be refined satisfactorily. Crystals of [Ru$_2$(μ-F)$_3$-(PEt$_3$)$_6$](OTf)·0.5THF were grown similarly. There are two independent molecules in the unit cell. The binuclear Ru ⋯ Ru cation consists of two Ru(PEt$_3$)$_3$ units bridged symmetrically by three fluorine atoms (Fig. 2). The Ru–F bond lengths (Table 2) range from 2.1315(18) to 2.1702(19) Å, very close to
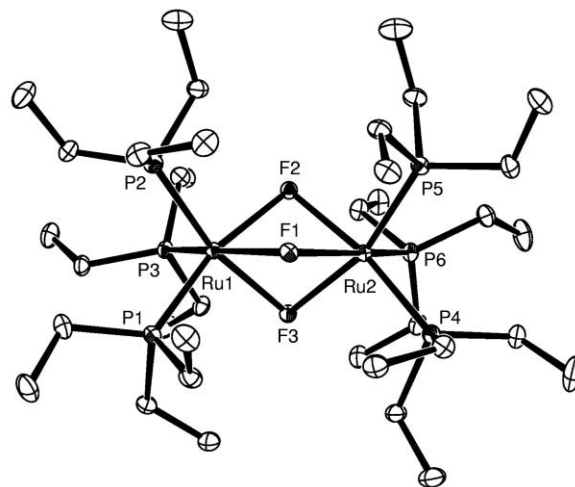

Fig. 2 ORTEP[31] diagram of one of the two independent cations in [Ru$_2$(μ-F)$_3$(PEt$_3$)$_6$](CF$_3$SO$_3$)·0.5THF. Ellipsoids are drawn at the 30% level.

Table 3 CH microanalysis for the complexes $[Ru_2(\mu\text{-}F)_3(PR_3)_6]FHF$

Element	$[Ru_2(\mu\text{-}F)_3(PEt_3)_6]FHF$ $C_{36}H_{91}F_5P_6Ru_2$		$[Ru_2(\mu\text{-}F)_3(P^nPr_3)_6]FHF$ $C_{54}H_{127}F_5P_6Ru_2$		$[Ru_2(\mu\text{-}F)_3(P^nBu_3)_6]FHF$ $C_{72}H_{163}F_5P_6Ru_2$	
	Calc.	Found	Calc.	Found	Calc.	Found
%C	42.93	42.55	51.49	51.1	57.19	57.27
%H	9.11	9.28	10.16	10.23	10.87	10.52

the values in the literature and significantly longer than in any terminal fluoride complex.[1,19,21] The Ru–F–Ru angles vary from 91.72(7) to 93.02(7)°. The F–Ru–F angles vary from 73.03(7) to 74.46(7)°. The Ru ⋯ Ru distance is 3.1081(4) Å in one of the two independent cations and 3.1031(4) Å in the other cation. Overall, the structure is very similar to that reported by Crabtree *et al.* of $[\{MoH_2(PMePh_2)_3\}_2(\mu\text{-}F)_3]^+$.[23] The F–Ru–F angles are in the range listed for comparable cyclic complexes by Roesky and Haiduc, but the Ru–F–Ru angles are smaller than for other transition metal fluorides.[21]

Discussion and conclusions

The complexes *cis*-$[RuH_2(PR_3)_4]$ (R = Et, Pr, Bu) behave differently towards $NEt_3\cdot3HF$ from *cis*-$[RuH_2(PMe_3)_4]$ or *cis*-$[RuH_2(diphos)_2]$. With the larger alkyl substituents, loss of phosphine occurs, opening up the formation of dinuclear cations. This synthesis is straightforward and offers a fairly general approach to previously unknown fluoride-bridged diruthenium species. A related cation, $[Ru_2(\mu\text{-}F)_3(PMe_2Ph)_6]^+$, has been reported, but no analytical or spectroscopic data were provided to support the case.[27] We have been unable to locate any other publication concerning this species. Unlike $[\{M(CO)L_2\}_2(\mu\text{-}F)_3]^+$ (M = Ru, Os), $[Ru_2(\mu\text{-}F)_3(PR_3)_6]^+$ complexes have proved extremely stable. For instance, the cation with R = PEt_3 is stable to KCl, KBr, KI, CH_3I, Et_3SiH, sodium naphthalenide, triethylamine, HCl in diethyl ether and Ag^+ in acetone. These complexes are not stabilised by push–pull interactions as suggested in ref. 5, but the bridging coordination mode prevents nucleophilic attack since the fluoride is less nucleophilic when acting as a three-electron donor. Thus stabilisation of late transition metal fluoride complexes can also be achieved by control of the coordination mode. Initially, the counter-ion generated in the synthesis is $[F(HF)_n]^-$; spectroscopic distinction of the free ion from a coordinated $F(HF)_n$ ligand is not trivial considering that there are also complexed fluoride ligands present in the cation. However, salt metathesis reactions provide a decisive demonstration that the $F(HF)_n$ moiety is present simply as an anion.

The formation of $[Ru_2(\mu\text{-}F)_3(PR_3)_6]^+$ may be initiated by protonation of the dihydride and formation of $[Ru(FHF)_2(PR_3)_4]$ as for the PMe_3 complex.[24] Presumably, these complexes are labile with respect to loss of phosphine when R = Et, Pr, Bu. The free phosphine may act as a base and assist in removal of HF. Any coordinatively unsaturated species will initiate formation of the dinuclear complex. Our results show the extreme sensitivity of the fluorination reactions to changes in the phosphine and the versatility of $NEt_3\cdot3HF$ as a reagent for synthesising late transition metal fluoride complexes.

A series of chloride-bridged analogues, $[Ru_2(\mu\text{-}Cl)_3(PR_3)_6]^+$, have been known for many years. Recently, Knottenbelt *et al.* have shown by DFT calculations that the Ru ⋯ Ru distance in these ions is strongly influenced by the steric demands of the phosphine and that the steric effects may even induce different ground states in the oxidised ions $[Ru_2(\mu\text{-}Cl)_3(PR_3)_6]^{3+}$ according to the choice of phosphine.[28] The Ru ⋯ Ru distance in the fluoride complex is considerably shorter than in any of the chloride-bridged species. It is not yet clear whether the fluoride-bridged complexes will be as sensitive to steric effects.

Experimental

The complexes *cis*-$[RuH_2(PR_3)_4]$ (where R = ethyl, propyl and butyl) were prepared according to the literature (56–70% yields).[29] The hydride complexes were dissolved in THF and a two-fold excess of $NEt_3\cdot3HF$ was added to the solutions to give dihydrogen and a yellow product $[Ru_2(\mu\text{-}F)_3(PR_3)_6][F(HF)_n]$. The reactions took 3 h to reach completion. Hydrogen bubbles formed for the first few minutes. The products were recrystallised from THF at −25 °C to give yellow crystals, yield 56–66%. Salt metathesis was carried out by stirring THF solutions of the salts with KPF_6 or NH_4OTF at room temperature. Analytical data are shown in Table 3.

Mass spectra (FAB-MS): $[Ru_2(\mu\text{-}F)_3(PEt_3)_6][F(HF)_n]$: *m/z* 969 (100%, M^+), 822 (12%), 475 (16%).

$[Ru_2(\mu\text{-}F)_3(PPr_3)_6][F(HF)_n]$: *m/z* 1220 ($M^+$), 825, 600.

$[Ru_2(\mu\text{-}F)_3(PBu_3)_6][F(HF)_n]$: *m/z* 1474 ($M^+$), 1214, 727.

IR (Nujol, cm^{-1}):

$[Ru_2(\mu\text{-}F)_3(PEt_3)_6][F(HF)_n]$: 1461 (s), 1377 (s), 1346 (s), 1270 (sh), 1258 (m), 1234 (sh), 1033 (s), 971 (s), 752 (s), 604 (m), 499 (w), 447 (m), 374 (m).

$[Ru_2(\mu\text{-}F)_3(P^nPr_3)_6][F(HF)_n]$: 1458 (s), 1367 (s), 1339 (s), 1272 (w), 1262 (m), 1249 (sh), 1033 (m), 980 (m), 752 (s), 609 (m), 502 (w), 449 (w), 374 (vw).

$[Ru_2(\mu\text{-}F)_3(P^nBu_3)_6][F(HF)_n]$: 1468 (s), 1342 (m), 1239 (w), 1232 (w), 1093 (s), 1034 (m), 1007 (m), 972 (m), 904 (m), 892 (sh), 752 (sh), 464 (m), 380 (m), 327 (vw).

Diffraction data were collected for a block of dimensions 0.35 × 0.20 × 0.15 mm on a Stöe IPDS-II diffractometer. The structure was solved by direct methods (SHELXS) and refined against F^2 (SHELX97).[30] $[Ru_2(\mu\text{-}F)_3(PEt_3)_6][CF_3SO_3]\cdot0.5THF$, $C_{39}H_{94}F_6O_{3.5}P_6Ru_2S$, $M = 1153.16$, triclinic, $P\bar{1}$ $a = 14.8900(14)$, $b = 19.5384(17)$, $c = 21.205(2)$ Å, $a = 106.410(7)°$, $\beta = 106.800(7)°$, $\gamma = 103.127(7)°$, $V = 5286.1(8)$ Å^3, $T = 150$ K, $Z = 4$, $D_c = 1.449$ Mg m^{-3}, $\mu = 0.848$ mm^{-1}, $F(000) = 2416$, reflections measured 116744, unique 41199 ($R_{int} = 0.0656$), $R1 = 0.0503$ on $I > 2\sigma(I)$, $wR2 = 0.1267$ (all data). There are two independent molecules in the asymmetric unit. The tetrahydrofuran molecule is disordered over two positions. Occupancy was refined and found to be 50% in each position. All H-atoms were added at calculated positions and refined using a riding model. All non H-atoms were refined anisotropically. Structures were visualised with ORTEP-3 for Windows.[31]

CCDC reference number 191709.

See http://www.rsc.org/suppdata/dt/b3/b301582c/ for crystallographic data in CIF or other electronic format.

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