

# Heteropolymetallic complexes of 1,1'-bis(diphenylphosphino)ferrocene, dppf

## IX. Electrochemical oxidation of the dicopper(I) complex cation $[(\mu\text{-dppf})(\text{Cu}(\text{dppf}))_2]^{2+}$ . A multi-electron redox system

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### Abstract

The electrochemical oxidation of the homoleptic dimeric complex  $[(\mu\text{-dppf})(\text{Cu}(\text{dppf}))_2]^{2+}$  (dppf = 1,1'-bis(diphenylphosphino)ferrocene) at a platinum electrode in 1,2-dichloroethane was studied by cyclic voltammetry and controlled potential electrolysis. The compound was found to undergo an apparently reversible single-stepped three-electron transfer process involving the three non-interacting ferrocene moieties. The electrogenerated pentacation was, however, unstable towards fragmentation into the fairly stable Cu(I)(dppf<sup>•+</sup>) complex,  $[\text{Cu}(\text{dppf})]^{2+}$ , and the fugitive bis(diphenylphosphino)ferrocenium radical cation,  $[\text{dppf}]^{•+}$ , the ultimate fate of which was the formation of protonated and oxygenated dppf derivatives upon reaction with water present in the reaction medium. Subsequent back-reduction restored the starting dimer and produced the novel complex  $[\text{Cu}(\text{dppf})(\text{dppfO})]^+$ , which was characterized by <sup>31</sup>P NMR spectroscopy.

### Introduction

Considerable attention has been focused on the synthesis and chemistry of heterobi-(or poly-)metallic complexes in recent years. This interest stems primarily from the possibility that two or more adjacent, non-directly bonded, different metal centres should be able to disclose novel cooperative chemical properties. 1,1'-Bis(diphenylphosphino)ferrocene (dppf) revealed to be a remarkably simple metal-bearing ligand suitable for preparing bi- and polymetallic compounds with various degrees of structural complexity [1]. Moreover, the presence in the relevant metal complexes of the versatile and one-electron reversible redox centre, ferrocene, makes them potentially interesting from the electrochemical point of view. As a matter of fact, changes in the oxidation state of the pendant organometallic ligand should influence the electron density in the central metal without changing the immediate coordination sphere, thus offering the perspective of a tunable control of the metal reactivity in complexes containing ferrocenyl-derived ligands.

As parts of our current studies on the coordinating ability of dppf [1e, f, i, j], we recently reported the synthesis and the solution chemistry of the homoleptic

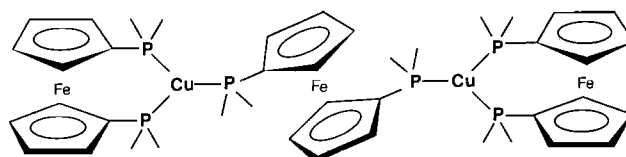


Fig. 1. Schematic drawing of the structure of the dication dimer  $[(\mu\text{-dppf})(\text{Cu}(\text{dppf}))_2]^{2+}$ .

complexes  $[(\mu\text{-dppf})(\text{Cu}(\text{dppf}))_2]\text{X}_2$  ( $\text{X} = \text{BF}_4^-$ ,  $\text{ClO}_4^-$ ) [1k] as well as the single crystal X-ray characterization of the perchlorate salt [1]. A comprehensive investigation on the electrochemical behaviour of dppf has also been previously described [2]. Reported herein is the electrochemical oxidation of the cationic moiety  $[(\mu\text{-dppf})(\text{Cu}(\text{dppf}))_2]^{2+}$  (see Fig. 1), which belongs to the group of interesting multi-electron redox systems.

### Experimental

#### Materials

The complex  $[(\mu\text{-dppf})(\text{Cu}(\text{dppf}))_2](\text{BF}_4)_2$  was prepared as described elsewhere [1k]. Anhydrous 1,2-dichloroethane (DCE) was purchased from Aldrich and used as received. The electrolyte tetrabutylammonium hexafluorophosphate (TBAH) was recrystallized twice

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from ethyl acetate and dried *in vacuo* at 60 °C prior to use. All other chemicals were of reagent-grade quality and were used without further purification. High-purity argon, further purified from oxygen by passage over reduced copper at 450 °C, was used in the electrochemical experiments. Syntheses and manipulation of solutions were performed under nitrogen by standard Schlenk-line techniques.

#### Apparatus and procedure

All experiments were performed on anhydrous, deoxygenated, DCE solutions with 0.2 M TBAH as the supporting electrolyte, using a conventional three-electrode liquid-jacketed cell. Cyclic voltammetry measurements were performed with an Amel 551 potentiostat modulated by an Amel 566 function generator, and the recording device was a Hewlett-Packard 7090 A measurements plotting system. The working electrode was a planar platinum microelectrode (*c.* 0.3 mm<sup>2</sup>) surrounded by a platinum spiral counter electrode.

Controlled potential electrolyses were performed with an Amel 552 potentiostat linked to an Amel 731 digital integrator. The working electrode was a platinum gauze (*c.* 100 cm<sup>2</sup>) and the counter electrode was an external mercury pool, the connection being made through an appropriate salt bridge.

In all cases a silver/0.1 M silver perchlorate in acetonitrile, separated from the test solution by 0.2 M TBAH in DCE solution sandwiched between two fritted disks, was used as the reference electrode. Compensation for *iR* drop was achieved by positive feedback. Ferrocene was added at the end of each experiment as an internal reference. All potentials are referred to the ferrocenium/ferrocene couple ( $E^\circ = +0.120$  V relative to the actual Ag/AgClO<sub>4</sub> reference electrode).

<sup>1</sup>H and <sup>31</sup>P NMR spectra were recorded on Jeol 90 Q and Bruker AM 400 spectrometers equipped with a variable temperature apparatus and were referenced to internal SiMe<sub>4</sub> and external H<sub>3</sub>PO<sub>4</sub> (85% wt./wt.), respectively.

#### Electrochemical synthesis of [Cu(dppf)(dppfO)](PF<sub>6</sub>)

A solution of [(μ-dppf)(Cu(dppf))<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (0.700 g, 0.356 mmol) in DCE (50 ml), 0.5 M TBAH, was electrolyzed at 0.7 V versus Ag/0.1 M AgClO<sub>4</sub> acetonitrile electrode in a two-compartment cell on a platinum gauze electrode and a mercury pool counter-electrode at 0 °C. After removal of 3 mol of electrons per mole of complex, the resulting intense greenish solution was exhaustively electrolyzed at -1.6 V by simply inverting the polarity of the electrodes and then evaporated to dryness under reduced pressure. The residue was extracted with 50 ml of hot methanol and the extract filtered off to leave 0.34 g (0.163 mmol) of [(μ-dppf)(Cu(dppf))<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> as yellow powder. The or-

ange filtrate was then cooled to -20 °C to precipitate most of TBAH. After filtering off TBAH, the mother liquor was concentrated *in vacuo* to *c.* 10 ml and allowed to stand overnight at -20 °C to deposit orange-yellow microcrystals of the product, which were filtered off, washed with hot ethyl acetate and dried under vacuum (0.21 g, 0.157 mmol). Its identity was checked by elemental analysis and <sup>31</sup>P NMR spectroscopy. *Anal.* Calc. for C<sub>68</sub>H<sub>56</sub>CuF<sub>6</sub>Fe<sub>2</sub>OP<sub>5</sub>: C, 61.26; H, 4.23. Found: C, 61.44; H, 4.30%. <sup>31</sup>P{<sup>1</sup>H} NMR (161.98 MHz) in CD<sub>2</sub>Cl<sub>2</sub> at -40 °C, δ (ppm): 35.16 (triplet, <sup>3</sup>J<sub>PP</sub> 8.5 ± 0.5 Hz, P(O)<sub>(dppfO)</sub>); -8.6 (triplet, <sup>2</sup>J<sub>PP</sub> 92 Hz, P<sub>(dppfO)</sub>); -15.91 (doublet, <sup>2</sup>J<sub>PP</sub> 92 Hz, 2P<sub>(dppf)</sub>); -144.5 (septuplet, <sup>1</sup>J<sub>PF</sub> 707 Hz, PF<sub>6</sub><sup>-</sup>). <sup>1</sup>H NMR (89.55 MHz) in CD<sub>2</sub>Cl<sub>2</sub> at 27 °C, δ: 7-7.7 (complex multiplet, C<sub>6</sub>H<sub>5</sub>, 40H); 4.47 (singlet, C<sub>5</sub>H<sub>4</sub>, 8H); 4.26 (singlet, C<sub>5</sub>H<sub>4</sub>, 4H); 4.21 (singlet, C<sub>5</sub>H<sub>4</sub>, 4H).

Addition of excess dppf (0.10 g, 0.180 mmol) in toluene (20 ml) to the filtrate, containing the unreacted [Cu(dppf)]<sup>+</sup> solvento complex, resulted in the precipitation of additional [(μ-dppf)(Cu(dppf))<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (0.15 g, 0.072 mmol).

## Results and discussion

A representative cyclic voltammogram of the title compound recorded at 25 °C in DCE 0.2 M TBAH is depicted in Fig. 2. Under these conditions the complex appears to be oxidized in a single uncomplicated reversible step with a potential value ( $E_{1/2} = 0.465$  V, as a mean value of the potentials for anodic and cathodic peak currents) considerable more anodic than that displayed by the uncoordinated ligand ( $E_{1/2} = 0.183$  V) [2], but significantly less positive than those we previously found in the ferrocenyl-based oxidations of Pd(II) and Pt(II) dppf derivatives (0.65 V <  $E_{1/2}$  < 0.75 V) [1f]. Interestingly, the Cu(I) ion, when complexed by dppe (dppe = 1,2-bis(diphenylphosphino)ethane) displays under identical experimental conditions an essentially reversible redox activity centered at  $E_{1/2} = 0.610$  V [3], thus raising the question as to whether the metal or the dppf ligand is the species that undergoes removal of electrons. On the other hand, in a statistically regulated redox system the separation of anodic and cathodic peak in the cyclic voltammetry profile for a single-stepped three-electron charge transfer reaction should be the same, within 1 mV, as predicted for a single-stepped two-electron process, i.e. 57 and 58.5 mV, respectively [4, 5]. The cyclic voltammogram of the title complex shows a peak separation of 80 mV, a value which is only slightly larger than that expected for a multistep electron transfer reaction regulated only by statistical effects. This might signal extremely weak electronic interactions between the redox sites and

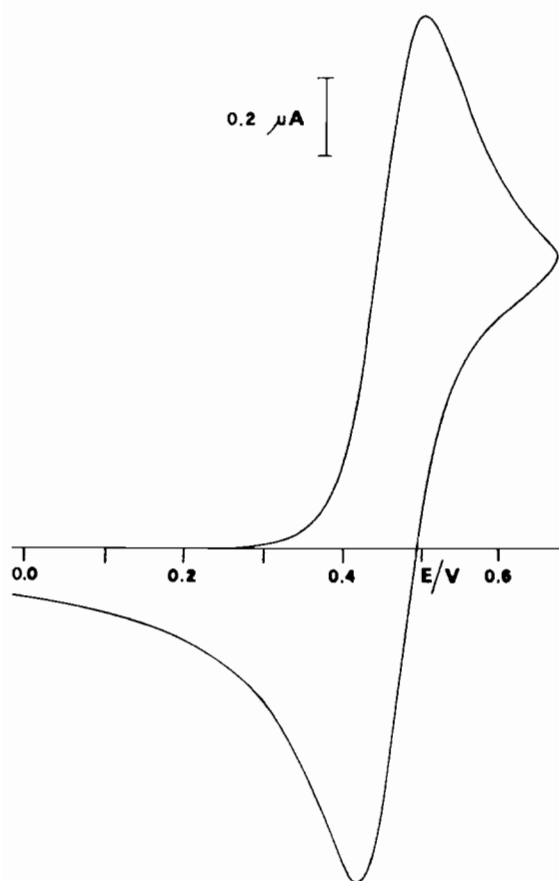


Fig. 2. Cyclic voltammogram for oxidation of 1.07 mM  $[(\mu\text{-dppf})(\text{Cu}(\text{dppf}))_2]^{2+}$  in DCE, 0.2 M TBAH, at 25 °C (scan rate 0.2 V s<sup>-1</sup>).

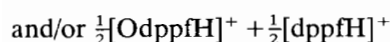
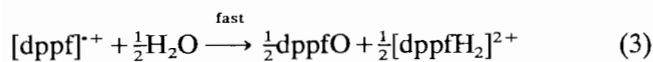
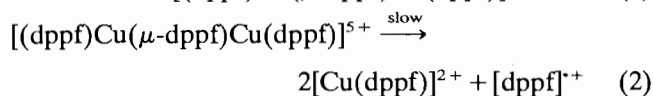
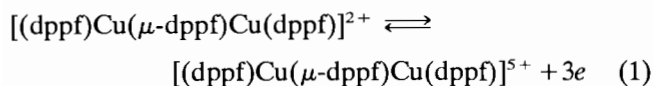
reveals that electrons are exchanged almost in a single shot, but it does not allow one to determine whether the redox process takes place at the dppf ligands (3e) or at the copper atoms (2e). A comparison with the cyclic voltammetric responses of the strictly related complexes  $[(\mu\text{-X})\text{M}(\text{dppf})_2]^{2+}$  (M = Pd or Pt; X = Cl<sup>-</sup> or OH<sup>-</sup>), all of which undergo reversible two-step one-electron charge transfer reactions involving the two non-interacting ferrocene moieties [1f], shows that under identical conditions the oxidation peak current for the dicopper complex is *c.* 1.4 times as high as exhibited by the dipalladium and -platinum derivatives. This result seems to support the process to be localized on the dppf ligands. No clear second oxidation wave associated with Cu is observed when the potential is scanned up to the positive solvent limit.

Confirmatory evidence in favour of ferrocene-centred oxidation is provided by the course of controlled potential coulometry experiments. Exhaustive electrolysis carried out at 25 °C and at potentials past the anodic peak results in the removal of 3 mol of electrons per mole of depolarizer to give an intense greenish solution with a voltammetric reduction profile corresponding

virtually to the oxidation pattern of the precursor, except for a small negative shift in  $E_{1/2}$  value (*c.* 20 mV) and for *c.* 30% lowering of the peak current. The analyte is not stable indefinitely: in the long run (hours) the solution turns from greenish to dark brown colour with contemporary flattening of the voltammetric signal distinctive of the primary oxidation product, likely through a reaction with trace amounts of water as suggested by the greatly increased decomposition rate (within minutes) when H<sub>2</sub>O is deliberately added.

At lower temperature, 0 °C, exhaustive electrolyses confirm the removal of three electrons/dimer and lead to final greenish, quite stable, solutions showing voltammetric features virtually identical with those described above, *i.e.* a redox couple centred at  $E_{1/2} = 0.440$  V with only slightly smaller (*c.* 85%) peak currents relative to the parent compound. The UV-Vis spectrum of the resulting solution displays three absorption bands at  $\lambda_{\text{max}} = 772, 588(\text{sh})$  and 430 nm. The strong similarity between this spectrum and that exhibited by the Pt(II) bis(phosphino)ferrocenium cation,  $[(\text{dppf})\text{PtCl}_2]^+$ , in nitromethane [6] substantiates the assignment of the oxidation product as the copper(I) complex of the  $[\text{dppf}]^+$  ligand. Immediate back-reduction of this analyte results in the consumption of 2 mol of electrons per mole of starting dimer in the original solution to yield an orange-yellow solution whose voltammetric pattern is that expected for an uncomplicated reversible electron transfer reaction, and virtually identical with that of  $[(\mu\text{-dppf})(\text{Cu}(\text{dppf}))_2]^{2+}$ , apart from the small negative shift in the  $E_{1/2}$  value. Cyclic voltammetry inspection in the cathodic region past 0.0 V reveals the presence of new reductive signals attributable to protonated dppf derivatives by analogy to their redox behaviour [2]. The subsequent electrochemical reduction at -1.5 V, past the proton-based waves, requires just the expected additional amount of charge and restores completely the original voltammetric picture.

In the light of our previous findings on the electrochemical oxidation of the uncoordinated ligand [2], the water-promoted formation of oxygenated and, as a consequence of protonated, dppf derivatives strongly suggests that upon removal of electrons the dimeric complex undergoes initial fragmentation reaction into the fairly long-lived  $[\text{Cu}(\text{dppf})]^{2+}$  moieties and the fugitive bis(phosphino)ferrocenium radical ion,  $[\text{dppf}]^+$ , the ultimate fate of this latter being the already ascertained formation of oxygenated and protonated products upon nucleophilic attack by water present in the reaction medium. Hence, the whole of the electrochemical and chemical observations points convincingly to the reaction sequence shown in eqns. (1)–(3)



where the monomeric, likely  $\text{PF}_6^-$  ion- or solvent-assisted, species  $[\text{Cu}(\text{dppf})]^{2+}$  would be responsible for the reversible reduction centred at  $E_{1/2} = 0.440$  V and the terms fast and slow refer to the cyclic voltammetry time scale and  $0^\circ\text{C}$ . Control experiments reveal that  $[\text{Cu}(\text{dppf})(\text{CH}_3\text{CN})_2]^+$ , generated *in situ* by mixing  $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$  and dppf in 1:1 ratio, exhibits indeed a uncomplicated reversible one-electron oxidation at  $E_{1/2} = 0.430$  V.

Moreover, chronoamperometric tests indicate that the value of the diffusion coefficient of the monomer complex is roughly 1.7 times as high as that of the dimer one, thus allowing the deceiving sequence of peak currents observed in the oxidation–reduction cycle to be properly rationalized. Obviously, the confirmation of the proposed mechanism awaited the detection of hidden bisphosphine monoxide, dppfO, in the final solution. This gap is filled by the recovery of the starting dication as the hexafluorophosphate salt and of the new complex  $[\text{Cu}(\text{dppf})(\text{dppfO})](\text{PF}_6)$ , in the appropriate 1:1 molar ratio, at the end of three-electron oxidation and back-reduction pathways in the bulk electrolysis experiment (see ‘Experimental’). Of course, the initially formed, coordinatively unsaturated,  $[\text{Cu}(\text{dppf})]^+$  reacts with dppf and dppfO as soon as they are generated at the electrode, converting into the stable  $[(\mu\text{-dppf})(\text{Cu}(\text{dppf}))_2]^{2+}$  and  $[\text{Cu}(\text{dppf})(\text{dppfO})]^+$ , respectively. As the redox patterns of uncoordinated dppfO and dppf are quite similar [2], it is conceivable that the two ligands keep this similarity upon coordination to the metal. This would make their adducts undistinguishable from the electrochemical point of view.

The novel compound  $[\text{Cu}(\text{dppf})(\text{dppfO})]^+$  is, to the best of our knowledge, the first example of a metal complex containing the P and/or O donor dppf monoxide ligand. The solution  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum recorded at 36.23 MHz and at room temperature exhibits three sets of resonances: a poorly resolved triplet centred at 34.60 ppm and a broad multiplet in the range from  $-5$  to  $-15$  ppm attributable to the dppf and dppfO ligands, in addition to the sharp binomial septuplet ( $\delta -144.5$ ,  $^1J_{\text{PF}} 707$  Hz) due to the  $\text{PF}_6^-$  anion. Lowering the temperature causes a better resolution of the resonances of the two ligands. Figure 3 represents the

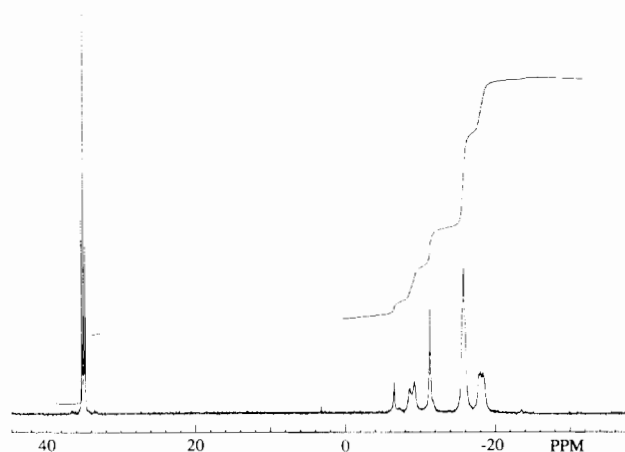


Fig. 3.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at 36.23 MHz of  $[\text{Cu}(\text{dppf})(\text{dppfO})](\text{PF}_6)$  in  $\text{CD}_2\text{Cl}_2$  at  $-95^\circ\text{C}$ .

spectrum recorded at  $-95^\circ\text{C}$  in this spectral region. The sharp triplet at lower fields ( $\delta 35.0$ ) is clearly attributable to the P(O) phosphorus atom of the coordinated dppfO ligand. This resonance, in fact, occurs only a few ppm at lower field in comparison with that observed for the corresponding atom in the uncoordinated bis(phosphine) monoxide ( $\delta_{\text{P(O)}} 28.5$  and  $\delta_{\text{P}} -17.4$ ) [2]. The second order multiplet ( $\delta -6.5$  to  $-18.2$ ), the total intensity of which is three times that of the P(O) resonance, is consistent with the presence of three P(III) atoms bonded to the metal centre. Although some resonances appear still unresolved, this multiplet is reminiscent of the  $\text{AB}_2$  pattern exhibited by the related complex  $[(\mu\text{-dppf})(\text{Cu}(\text{dppf}))_2]^{2+}$  in its  $^{31}\text{P}$  NMR spectrum [1k]. In this dinuclear species, whose structure was determined by diffraction methods [11], the two chemically nonequivalent phosphorus atoms exhibited a chemical shift difference of 2.5 ppm and a  $^2J_{\text{P(A)P(B)}}$  of 95 Hz. These observations suggest that, at low temperature, both the dppf and dppfO ligands are bonded to the metal centre in a bidentate fashion, allowing tetrahedral coordination to be attained by the copper(I) ion. The fact that the P(O) resonance occurs as a 1:2:1 triplet is indicative that the phosphorus atom is coupled with two magnetically equivalent nuclei, and therefore the dppf ligand has to be symmetrically coordinated to the metal centre. The unobserved magnetic interaction between the P(V) and P(III) nuclei of the dppfO moiety could arise from a unfavorable angle between the two phosphorus atoms making the  $^3J_{\text{PP}}$  value too small to be detected. The whole of these observations and considerations is confirmed by the  $^{31}\text{P}$  NMR spectrum recorded at 161.98 MHz and low temperature. As shown in Fig. 4, while the lower field triplet appears unchanged, the  $\text{AB}_2$  multiplet occurs as an approximate first order  $\text{AX}_2$  pattern, from which

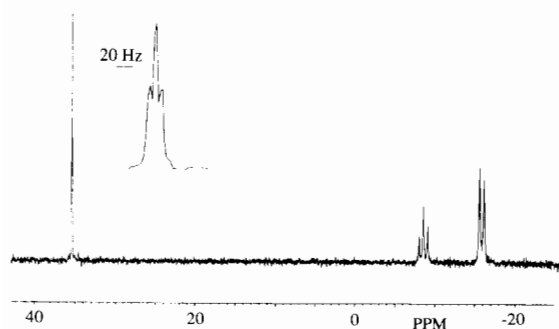


Fig. 4.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at 161.98 MHz of  $[\text{Cu}(\text{dppf})(\text{dppfO})](\text{PF}_6)$  in  $\text{CD}_2\text{Cl}_2$  at  $-40^\circ\text{C}$ .

the  $^2J_{\text{PP}}$  (92 Hz) is immediately evident. Although the temperature dependence of the NMR bis(phosphine) resonances was not investigated in detail, it seems related to a partial dissociation of one of the Cu–P bonds, which would become significant at room temperature on the NMR time scale.

As a conclusion, we want to report here a comment on the  $E_{1/2}$  value relevant to the title compound redox couple. On the assumption of a merely statistical control, the measured  $E_{1/2}$  corresponds exactly to the release/uptake of the second of the three electrons, the one process which is not affected by statistical terms. The first and the third one-electron steps should take place at  $E_1 = E_{1/2} - 28.2$  mV and  $E_3 = E_{1/2} + 28.2$  mV (at  $25^\circ\text{C}$ ), respectively [4].

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