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Reactions of the technetium(V) phenylimido complex $[TcX_3(NPh)(PPh_3)_2]$ with aromatic thiolate ligands (where X = Cl, Br)

Terrence Nicholson*, Jessica Cook, Alan Davison and Alun G. Jones
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139 (USA)
and Department of Radiology, Harvard Medical School and Brigham and Women's Hospital, Boston, MA 02215 (USA)

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Abstract

The reaction of $KTcO_4$ with triphenylphosphine and 1-acetyl-2-phenylhydrazine in methanol with HBr gives the Tc(V) phenylimido complex $[TcBr_3(NPh)(PPh_3)_2]$, analogous to the published reaction with HCl. The phenylimido complex reacts with unsubstituted thiophenol and a proton scavenger (R_3N) in methanol to give the Tc(V) oxo complex $(R_3NH)[TcO(SPh)_4]$ in excellent yield. The IR spectrum of this complex shows an absorption at 936 cm^{-1} associated with $\nu(Tc{=}O)$. The Tc(V) complex $[TcCl_3(NPh)(PPh_3)_2]$ reacts with a four-fold excess of the sterically-hindered thiol 2,3,5,6-tetramethylbenzenethiol (TMBTH) and a proton sponge to give the Tc(V) complex $[Tc(NPh)(TMBT)_3(PPh_3)]$. The IR spectrum of this complex displays an absorption at 1100 cm^{-1} which is associated with $\nu(Tc{\equiv}N)$. The positive mode fast atom bombardment mass spectrum of this species displays an extensive fragmentation profile, including fragment of 947 *m/z*, which corresponds to the parent ion $[Tc(NPh)(TMBT)_3(PPh_3)]^+$. The analogous reaction with a five-fold excess of 2,6-dimethylbenzenethiol (DMBTH) and a proton sponge gives the anionic Tc(V) complex $(R_3NH)[Tc(NPh)(SAr)_4]$. The IR spectrum of this complex displays an absorption at 1100 cm^{-1} which is associated with $\nu(Tc{\equiv}N)$. The positive mode fast atom bombardment mass spectrum of this anionic species displays an extensive fragmentation profile, including fragments of 998 *m/z*, which corresponds to $\{(R_3NH)_2[Tc(NPh)(DMBT)_4]\}^+$ and 868 *m/z* which corresponds to $\{(R_3NH)[Tc(NPh)(DMBT)_4]\}^+$. The reaction of the Tc(V) complex $[TcCl_3(NPh)(PPh_3)_2]$ with the tetradentate phosphine-trithiol ligand $[P(C_6H_4\text{-}o\text{-}SH)_3]$, and a proton scavenger in methanol gives the neutral Tc(III) complex $[Tc(PPh_3)(PS3)]$. The FAB(+) mass spectrum of this complex shows the parent ion of 716 *m/z* and the peak associated with the fragment generated by the loss of the triphenylphosphine of 454 *m/z*. The IR spectrum shows no absorptions in either the region associated with $\nu(Tc{=}O)$ or $\nu(Tc{\equiv}N)$. The ^1H NMR spectrum of the diamagnetic Tc(III) complex shows only narrow-line signals associated with the aryl protons.

Key words: Technetium complexes; Imido complexes; Thiolate complexes

Introduction

The coordination chemistry of technetium has rapidly evolved in the past two decades. Recent advances include the synthesis of complexes which contain organonitrogen cores, including organodiazenido complexes (Tc=N=N–R) and organoimido complexes (Tc≡N–R) [1, 2]. These cores are unique in that they are capable of carrying with them organic substituents (–R) which allow the biodistributions of the species to be manipulated by altering the organic moiety bonded to the nitrogenous backbone. In addition, they can incorporate functional groups, which may be employed in the linking of biologically relevant molecules such as antibodies to technetium atoms [3].

The technetium(V) phenylimido complex $[TcCl_3(NPh)(PPh_3)_2]$ is isoelectronic to the Re(V) oxo complex $[ReOCl_3(PPh_3)_2]$, which is frequently used as a precursor in rhenium syntheses. The analogous Tc(V) oxo complex $[TcOCl_3(PPh_3)_2]$ is not isolable due to the facile oxygen abstraction of the second row transition metal, which is further reduced to the Tc(IV) species $[TcCl_4(PPh_3)_2]$ under the necessary reaction conditions. Nitrogen-based cores, such as the phenylimido core, are frequently less labile than their oxygen analogues. Thus, the Tc(V) phenylimido complex may prove to be a very useful synthetic intermediate in technetium chemistry. This has led us to question of the stability of the phenyl-

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*Author to whom correspondence should be addressed.

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imido–technetium interaction. Accordingly, we have been examining the substitution chemistry of $[\mathrm{TcCl_3(NPh)(PPh_3)_2}]$ with various ligand types. We report here the results of its reactions with various arylthiolates.

Experimental

Caution. Technetium-99 is a weak β^--emitter ($E = 0.292$ MeV, $t_{1/2} = 2.12 \times 10^5$ years). All work has been done in laboratories approved for the use of low levels of radioactive materials. Precautions have been detailed elsewhere [4]. Reagents and solvents were used as received unless otherwise stated.

Routine IR spectra were obtained on a Mattson Cygnus 100 FTIR spectrometer. Fast atom bombardment(+) spectra of samples dissolved in *p*-nitrobenzylalcohol matrix were recorded with a MAT 731 mass spectrometer equipped with an Ion Tech B11N FAB gun, operating at an accelerating voltage of 8 kV. The FAB gun produced a beam of 6–8 keV xenon neutrals. Analytical results were obtained from Atlantic Microlab Inc., Norcross, GA. Electronic spectra were recorded on a Hewlett Packard 8451A diode array spectrophotometer. ^{1}H NMR spectrum was recorded on a Varian XL-300 FTNMR spectrometer in $\mathrm{CD_2Cl_2}$ at room temperature. The phosphinetrithiol $\{\mathrm{P(C_6H_4\text{-}}o\mathrm{\text{-}SH)_3}\}$ was prepared by the literature method [5].

$[\mathrm{TcBr_3(NPh)(PPh_3)_2}]$ (*1*)

A 2 ml aqueous solution of ammonium pertechnetate (0.362 M) was combined with 0.05 g potassium hydroxide and evaporated to dryness with a rotary evaporator. The resulting white residue was then dissolved in 85 ml of methanol. To this was added 0.44 g of 1-acetyl-2-phenylhydrazine and 2.6 g triphenylphosphine and the resulting suspension was brought to reflux. The colorless suspension changed to a dull brown colored solution after 35 min of reflux at which time the heat was removed and the solution cooled to room temperature. To this was added 3 ml of 48% HBr and the solution stirred at room temperature for 15 min. Gradually a golden-brown colored solid formed which was isolated on a fine, fritted funnel. The product was washed with methanol and diethyl ether and dried under vacuum. Yield 70% (480 mg). *Anal.* Calc. for **1**, $\mathrm{TcBr_3P_2NC_{42}H_{35}}$: C, 52.86; H, 3.70; N, 1.47. Found: C, 52.56; H, 3.85; N, 1.67%. IR (KBr): $\nu(\mathrm{Tc{\equiv}N})$ 1088 cm^{-1}.

$(\mathrm{Pr_2EtNH})[\mathrm{TcO(SPh)_4}]$ (*2*)

A 296 mg sample of $[\mathrm{TcCl_3(NPh)(PPh_3)_2}]$ was suspended in 75 ml of methanol. To this was added a methanolic solution of 198 mg of thiophenol and 233 mg of diisopropylethylamine. The resulting suspension was stirred overnight at room temperature. The resulting red suspension was filtered, yielding a dark red–brown precipitate, which was washed with diethyl ether. The ether rinse was added to the filtrate which resulted in a additional amount of the desired precipitate. Yield 92% (226 mg). IR (KBr): 936 cm^{-1} $\nu(\mathrm{Tc{=}O})$. Electronic spectroscopy in acetonitrile ($\epsilon = 1$ mol^{-1} cm^{-1}); $\lambda_{\max}$ (nm) = 259 ($\epsilon = 5.25 \times 10^4$), 425 ($\epsilon = 5.70 \times 10^3$), 570 ($\epsilon = 3.30 \times 10^3$). *Anal.* Calc. for **2**, $\mathrm{TcS_4ONC_{32}H_{40}}$: C, 56.36*; H, 5.91; N, 2.05; S, 18.81. Found: C, 54.62; H, 6.01; N, 2.03; S, 17.84%. The calculated carbon percentage assuming quantitative formation of residual technetium carbide from the incomplete combustion of the sample is 54.60%, which quite closely corresponds to the experimental value of 54.62%.

$(\mathrm{Pr_2EtNH})[\mathrm{Tc(NPh)(SC_6H_3Me_2)_4}]$ (*3*)

A 143 mg sample of $[\mathrm{TcCl_3(NPh)(PPh_3)_2}]$ was suspended in 75 ml of methanol. To this was added a methanolic solution of 112 mg of diisopropylethylamine and 120 mg 2,6-dimethylbenzenethiol [6] (DMBTH). The yellow suspension was stirred at room temperature for 36 h. The resulting red–brown solution was evaporated to dryness with rotary evaporation and a solid was isolated with the addition of a minimum amount of methanol. Yield 55% (83 mg). IR (KBr): 1093 cm^{-1} $\nu(\mathrm{Tc{\equiv}N})$. FABMS(+): 998 *m/z*, $\{(\mathrm{Pr^i_2NEtH})_2[\mathrm{Tc(NPh)(DMBT)_4}]\}^+$; 927 *m/z*, $\{[\mathrm{Tc(NPh)(DMBT)_3}]_2\}^+$; 731 *m/z*, $\{(\mathrm{Pr^i_2NEtH})[\mathrm{Tc(NPh)(DMBT)_3}]\}^+$; 600 *m/z*, $[\mathrm{Tc(NPh)(DMBT)_3}]^+$; 464 *m/z*, $[\mathrm{Tc(NPh)(DMBT)_2}]^+$. *Anal.* Calc. for **4**, $\mathrm{TcS_4N_2C_{46}H_{61}}$: C, 63.56*; H. 7.07; N, 3.22; S, 14.75. Found: C, 62.08; H, 7.03; N, 3.12; S, 14.43%. The calculated carbon percentage assuming quantitative formation of residual technetium carbide is 62.18%, which quite closely corresponds to the experimental value of 62.08%.

$[\mathrm{Tc\{P(C_6H_4\text{-}}o\mathrm{\text{-}S)_3\}(PPh_3)}]$ (*4*)

A 75 mg sample of $[\mathrm{TcCl_3(NPh)(PPh_3)_2}]$ was suspended in 75 ml of methanol. To this was added a methanolic solution of 33 mg of $\{\mathrm{P(C_6H_4\text{-}}o\mathrm{\text{-}SH)_3}\}$ and 35 mg of diisopropylethylamine. The yellow suspension was stirred overnight at room temperature. A reddish brown solid was isolated and washed with cold methanol and dried under vacuum. The complex was recrystallized from methylene chloride layered with methanol. Yield 65% (43 mg). FABMS(+): 716 *m/z*, $[\mathrm{Tc(PPh_3)(PS3)}]^+$; 454 *m/z*, $[\mathrm{Tc(PPh_3)(PS3)}]^+$. *Anal.* Calc. for **5** as the monohydrate, $\mathrm{TcS_3P_2OC_{36}H_{29}}$: C, 58.84*; H, 3.98; S, 13.09. Found: C, 56.10; H, 3.90; S, 12.46%.

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*It has been previously noted in our research that results for carbon analyses are frequently off by one carbon, presumably a result of the formation of residual technetium carbide [6]

Results and discussion

We recently reported the synthesis of $[TcCl_3(NPh)(PPh_3)_2]$ from ammonium pertechnetate. It was later determined that the precursor employed in the reaction was not ammonium pertechnetate but the potassium salt. This subtle difference is critical to the success of the synthesis. The reagent employed to introduce the phenylimido unit is the disubstituted organohydrazine 1-acetyl-2-phenylhydrazine. It has since been shown that the ammonium ion is sufficiently acidic to protonate the phenyl-substituted nitrogen atom on the organohydrazine. The phenyl-bonded nitrogen is the more basic of the two hydrazine nitrogen atoms, a result of the electron releasing effect of the aryl group as compared to the electron withdrawing effect of the acetyl group. With the phenyl-nitrogen atom protonated, the lone pair of electrons is no longer capable of attacking the technetium ion, which is necessary for the formation of the phenylimido species. Consequently, the addition of a small amount of potassium hydroxide, prior to the evaporation of the aqueous pertechnetate solution, cleanly converts the ammonium ion to ammonia and water, leaving potassium pertechnetate, which reacts with the organohydrazine as suggested in the published mechanism. The reaction of potassium pertechnetate with 1-acetyl-2-phenylhydrazine and triphenylphosphine in methanol, followed by hydrogen bromide gives the analogous Tc(V) phenylimido complex with bromide ligands, $[TcBr_3(NPh)(PPh_3)_2]$. The IR spectrum and mass spectrometry results are directly analogous to those of the chloride complex. The only significant difference is the color, which is a dull red–brown, as compared to the green colored chloride complex.

The reaction of $[TcCl_3(NPh)(PPh_3)_2]$ with an excess of thiophenol and the proton scavenger diisopropylethylamine in methanol leads cleanly to the anionic Tc(V) oxo complex $(R_3NH)[TcO(SPh)_4]$. This species has been eluded to in the literature, but never fully reported. The original reference for this complex was a Ph.D. thesis, which utilized the reaction of $(Bu_4N)[TcOCl_4]$ with thiophenol and sodium hydroxide in methanol to generate the diamagnetic Tc(V) complex [7]. The work-up from this procedure was quite complicated and time consuming. The synthetic procedure reported here, which utilizes $[TcCl_3(NPh)(PPh_3)_2]$, is much simpler and gives better yields of analytically pure product. In the analogous rhenium chemistry, the complex $[ReO(SPh)_4]^-$ is so thermodynamically stable that, in the presence of excess thiophenol and base, most high oxidation state precursors react to give the diamagnetic Re(V) oxo tetrathiolate anion.

In the analogous reaction with the sterically hindered thiol 2,3,5,6-tetramethylbenzenethiol (TMBTH), the isolable but unstable product $[Tc(NPh)(TMBT)_3(PPh_3)]$ is generated from a two-phase reaction. Neither the technetium precursor nor the isolated product are methanol soluble. The IR spectrum of this product shows an absorption at 1090 cm^{-1}, which is the established region for the absorption of the $Tc{\equiv}N$ moiety as well as a weak absorption at 2940 cm^{-1} and a strong absorption in the 1400–1465 cm^{-1} region from the methyl groups of the arylthiolate ligand. This indicates that the phenylimido unit has been retained and that the tetramethylbenzene thiolate is present in the reaction product. No absorptions are present in the 900–1000 cm^{-1} region, which is the expected region for $\nu(Tc{=}O)$ from the expected contaminating byproduct, the anionic oxo–tetrathiolate complex $[TcO(SAr)_4]^-$. The FAB(+) mass spectrum of the neural Tc(V) complex shows a very detailed fragmentation profile, which is typical of technetium complexes containing these lipophilic, substituted thiophenylate ligands. The parent ion $[Tc(NPh)(TMBT)_3(PPh_3)]^+$ of 947 *m/z* units is observed as well as various fragments corresponding to the loss of the thiolate, phosphine and/or the phenylimido ligands. Other peaks include one of 1040 *m/z*, which corresponds to the fragment $[Tc_2(NPh)_2(TMBT)_4]^+$; a peak of 782 *m/z*, which corresponds to $[Tc(NPh)(TMBT)_2(PPh_3)]^+$ and a fragment of 685 *m/z*, which corresponds to $[Tc(NPh)(TMBT)_3]^+$. Additional peaks of 616 *m/z*, which is assigned as $[Tc(NPh)(TMBT)(PPh_3)]^+$; 520 *m/z*, which corresponds to $[Tc(NPh)(TMBT)_2]^+$; and 427 *m/z*, which is assigned to $\{[Tc(TMBT)_2]-2H\}^+$ are evident. Finally, peaks of 354 *m/z*, which corresponds to $\{[Tc(NPh)(TMBT)]-H\}^+$, and 263 *m/z*, which corresponds to $[Tc(TMBT)-H]^+$ are observed. Upon attempted recrystallization of this complex, the anionic oxo–tetrathiolate complex $(R_3NH)[TcO(TMBT)_4]$ is isolated, with the ammonium cation presumably still present from residual trialkylammonium chloride. The identity of this previously reported oxo complex was confirmed by IR and mass spectrometry. The instability of the phenylimido species in solution prevented us from obtaining an analytically pure sample and also made ^1H NMR spectroscopic analysis ambiguous. The inherent instability of the phenylimido complex is likely a reflection of both the enormous steric bulk surrounding the technetium atom from the three ortho-disubstituted phenylthiolate ligands and the triphenylphosphine as well as an inherent instability of the phenylimido core. Figure 1 gives a proposed structural representation of this complex. The isoelectronic, neutral Tc(V) oxo complex $[TcO(TMBT)_3(C_5H_5N)]$ has been structurally characterized and shown to contain a coordination geometry intermediate between square based pyramidal and trigonal prismatic [6].

An attempt was made to replace the triphenylphosphine of $[Tc(NPh)(TMBT)_3(PPh_3)]$ with a less

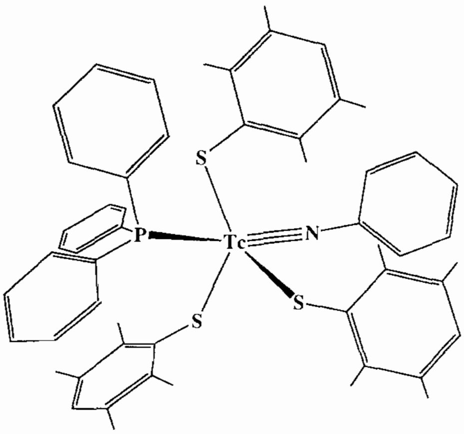

Fig. 1. Proposed structural representation of the isolable but unstable complex [Tc(NPh)(TMBT)$_3$(PPh$_3$)] displaying a coordination geometry intermediate between square pyramidal and trigonal bipyramidal.

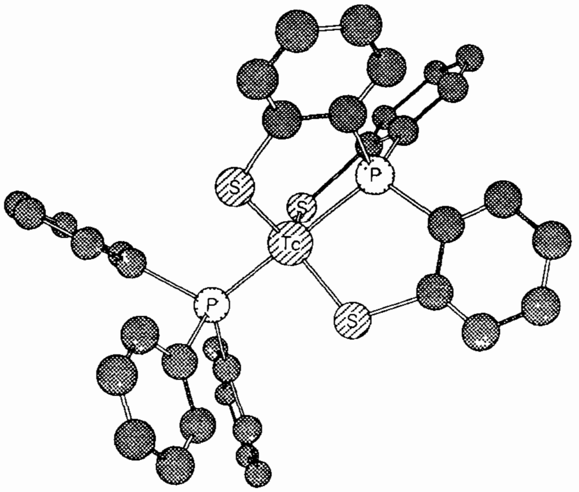

Fig. 2 Chem3D^{TM} structural representation of the neutral Tc(III) complex [Tc{P(C$_6$H$_4$-*o*-S)$_3$}(PPh$_3$)] formed from the reaction of [TcCl$_3$(NPh)(PPh$_3$)$_2$] and {P(C$_6$H$_4$-*o*-S)$_3$} with a proton scavenger.

bulky, neutral ligand to increase its solution stability and allow its recrystallization. The complex [Tc(NPh)(TMBT)$_3$(PPh$_3$)] was reacted with pyridine at room temperature in methanol. This reaction, however generates the Tc(V) complex [TcO(TMBT)$_3$(py)], with the oxo group again replacing the phenylimido moiety. The FAB(+) mass spectrum of this product displays the protonated parent ion {[TcO(TMBT)$_3$(py)]·H}$^+$ at 690 *m*/*z*. Other fragments corresponding to [Tc(TMBT)$_3$(py)]$^+$ at 673 *m*/*z*, [TcO(TMBT)$_3$]$^+$ at 610 *m*/*z*, [TcO(TMBT)$_2$(py)]$^+$ at 524 *m*/*z* and [TcO(TMBT)$_2$]$^+$ at 445 *m*/*z* are also observed.

By increasing the stoichiometric excess of hindered thiol from four to five, the reaction of [TcCl$_3$(NPh)(PPh$_3$)$_2$] with 2,6-dimethylbenzenethiol and a proton sponge gives the anionic Tc(V) complex (R$_3$NH)[Tc(NPh)(DMBT)$_4$]. This Tc(V) phenylimido complex is directly analogous to the anionic Tc(V) oxo complex (R$_3$NH)[TcO(SPh)$_4$]. The positive mode fast atom bombardment mass spectrum for this *anionic* complex shows the parent anion flying with two cations at 998 *m*/*z*, which corresponds to {(Pr$^i{}_2$NEtH)$_2$[Tc(NPh)(DMBT)$_4$]}$^+$. Also evident in the spectrum are signals at 927 *m*/*z*, which corresponds to the ion {[Tc(NPh)(DMBT)$_3$]$_2$}$^+$; 731 *m*/*z*, which corresponds to the ion pair {(Pr$^i{}_2$NEtH)[Tc(NPh)(DMBT)$_3$]}$^+$; 600 *m*/*z*, which corresponds to the fragment [Tc(NPh)(DMBT)$_3$]$^+$; and 464 *m*/*z*, which corresponds to the fragment [Tc(NPh)(DMBT)$_2$]$^+$. Attempted recrystallization of this complex again resulted in the isolation of the corresponding Tc(V) oxo-tetrathiolate anion, as determined by IR spectroscopy.

It has been previously reported that the rhenium complex [ReCl$_3$(NPh)(PPh$_3$)$_2$] reacts with the sterically hindered thiol 2,6-diisopropylphenylthiol in methanol to give the Re(V) anionic complex [Re(NPh)(SAr)$_4$]$^-$, however the characterization of this complex was never reported in the literature [8].

The reaction of [TcCl$_3$(NPh)(PPh$_3$)$_2$] with the tetradentate phosphinetrithiol {P(C$_6$H$_4$-*o*-SH)$_3$} and the proton scavenger diisopropylethylamine in methanol gives the neutral Tc(III) complex [Tc(PPh$_3$)(P{C$_6$H$_4$-*o*-SH}$_3$)]. This reaction also proceeds with the loss of the phenylimido unit, which is accompanied by a two-electron reduction from Tc(V) to Tc(III). The dark red–brown product is freely soluble in methylene chloride and can be recrystallized when layered with methanol. The FAB(+) mass spectrum shows the peak associated with parent ion of 716 *m*/*z* and the fragment generated from the loss of the triphenylphosphine of 454 *m*/*z*. The IR spectrum shows no absorptions in either the 1100 cm^{-1} region from ν(Tc≡N) or the 900–1000 cm^{-1} region from ν(Tc=O). The ^{1}H NMR spectrum consisting only of a complex multiplet of signals from phenyl protons of both ligands, in accordance with the stated structure. Figure 2 gives a structural representation of complex **4**.

Conclusions

We report here the reactions of the Tc(V) phenylimido complex [TcCl$_3$(NPh)(PPh$_3$)$_2$] with various arylthiolate ligands in methanol. The reaction with thiophenol gives the anionic species [TcO(SPh)$_4$]$^-$, which is cleanly isolated with the loss of the phenylimido core. The reaction with the more sterically hindered *ortho*-disubstituted benzene thiols allow isolation of the neutral Tc(V) phenylimido complex [Tc(NPh)(SAr)$_3$(PPh$_3$)] or the anionic complex (R$_3$NH)[Tc(NPh)(SAr)$_4$], depending on the stoichiometry of the thiolate employed. Attempted recrystallization of these complexes results in the isolation of the Tc(V) oxo-tetrathiolate anions. Reaction with the tetradentate phosphinetrithiol [P{C_6H_4-*o*-SH}$_3$) yields the neutral Tc(III) complex [Tc(PPh_3)(P{C_6H_4-*o*-S}$_3$)], also with the loss of the phenylimido unit. These results suggest that while the imido core is more thermodynamically stable than the isoelectronic oxo core, the kinetics involved in reactions in protic solvents may favor the exchange reaction with water to generate oxo containing products.

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