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Synthesis of Dimanganese Ruthenium Complexes from the Reaction of Ruthenium-Coordinated Thiophenes and Selenophene with [(1-Methylnaphthalene)Mn(CO)$_3$]BF$_4$ and Cp$_2$Co

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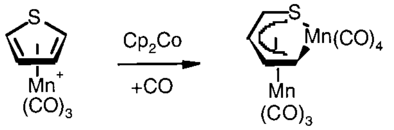
*Summary: Thiophene and selenophene derivatives of the ruthenium hexamethylbenzene dication have been synthesized, and their reaction with [(1-methylnaphthalene)-Mn(CO)$_3$]BF$_4$ (**2**) and Cp$_2$Co was studied. Treatment of [(η^5-C$_4$R$_4$S)Ru(η^6-C$_6$Me$_6$)]$^{2+}$ (**1**) with cobaltocene and [(1-methylnaphthalene)Mn(CO)$_3$]BF$_4$ (**2**) in CH$_2$Cl$_2$ at −78 °C led to the isolation of trimetallic (Mn$_2$Ru) thiophene complexes (η^6-C$_6$Me$_6$)Ru(SC$_4$R$_4$)Mn$_2$(CO)$_6$ (**3**). Similar treatment of the selenophene complex [(η^5-C$_4$H$_4$-Se)Ru(η^6-C$_6$Me$_6$)]$^{2+}$ gave the trimetallic (Mn$_2$Ru) selenophene complex (η^6-C$_6$Me$_6$)Ru(SeC$_4$R$_4$)Mn$_2$(CO)$_6$ (**9**). The X-ray structures of **3** and **9** show manganese inserted into a C−S or C−Se bond and two metal−metal bonds with no bridging carbonyls.*

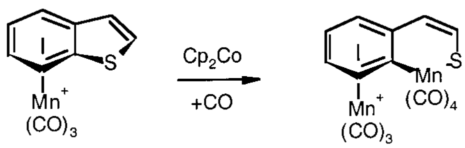
Introduction

The organometallic chemistry of thiophene has been extensively developed in order to provide models for the catalytic heterogeneous hydrodesulfurization (HDS) of thiophenic components of crude oil.[1] In HDS, attachment of the thiophenic substrate to the metal catalyst or activator and subsequent cleavage of the C−S bonds are key steps.[2] A number of methods are known for cleaving the C−S bonds such as insertion of a nucleophilic 14- or 16-electron organometallic fragment (oxidative insertion),[3] reductive insertion of an organometallic fragment,[4] reduction followed by electrophic addition,[5] and others.[6]

The use of cobaltocene as a reducing agent is quite common in organometallic chemistry.[5,7,8] Recently, it has been reported[9] that cobaltocene reduction of thiophenes or benzothiophenes coordinated to the Mn(CO)$_3$$^+$ moiety led to the formation of bimetallic metallacycles which contain a Mn(CO)$_4$ group regiospecifically inserted into a C−S bond (eqs 1, 2).



eq.1



eq.2

Herein we report that [(thiophene)Ru(C$_6$Me$_6$)]$^{2+}$ reacts with [(1-methylnaphthalene)Mn(CO)$_3$]BF$_4$ in the presence of Cp$_2$Co to give trimetallic complexes. The X-ray crystal structures of the trimetallic (RuMn$_2$) complexes show that a C−S bond has been cleaved.

Results and Discussion

Reaction of [(η^5-C$_4$R$_4$S)Ru(η^6-C$_6$Me$_6$)]$^{2+}$ (1) with [(1-CH$_3$C$_{10}$H$_7$)Mn(CO)$_3$]BF$_4$ (2) in the Presence of

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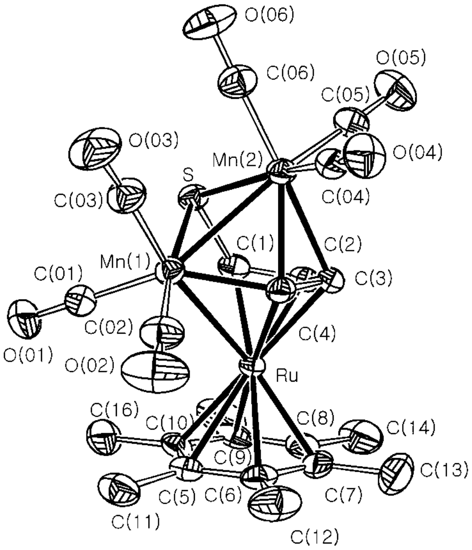
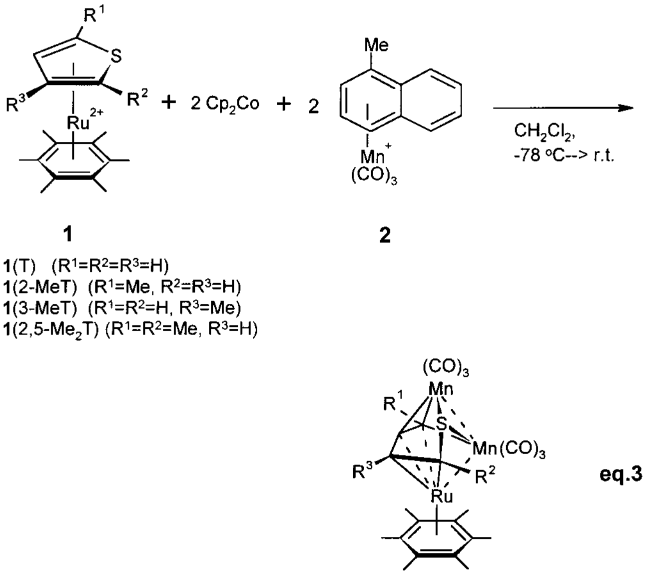


Figure 1. ORTEP drawing of **3**(T) with the atomic labeling scheme. Thermal ellipsoids are drawn at the 30% probability level.

Cp$_2$Co. Reaction of [(η^5-C$_4$R$_4$S)Ru(η^6-C$_6$Me$_6$)]$^{2+}$ (**1**) and [(1-methylnaphthalene)Mn(CO)$_3$]BF$_4$ (**2**) with cobaltocene in CH$_2$Cl$_2$ at −78 °C produced C−S cleaved trimetallic (Mn$_2$Ru) thiophene complexes **3** (eq 3), which we isolated in 22−25% yield. The ^{1}H NMR spectrum of **3**(2,5-Me$_2$T) showed two singlets at 3.16 (s) and 1.41 (s) ppm for two methyl groups, suggesting that one of the two C−S bonds may be cleaved. The ^{1}H NMR spectra of **3**(2-MeT) and **3**(3-MeT) showed only one methyl resonance, indicating regioselective cleavage of the C(5)−S bonds. The proposed C−S bond cleavage was confirmed by the X-ray structure determination of **3**(T) (Figure 1). The C−S cleavage occurs at the less hindered C−S bond.[5c,10]



1

1(T) (R^1=R^2=R^3=H)
1(2-MeT) (R^1=Me, R^2=R^3=H)
1(3-MeT) (R^1=R^2=H, R^3=Me)
1(2,5-Me$_2$T) (R^1=R^2=Me, R^3=H)

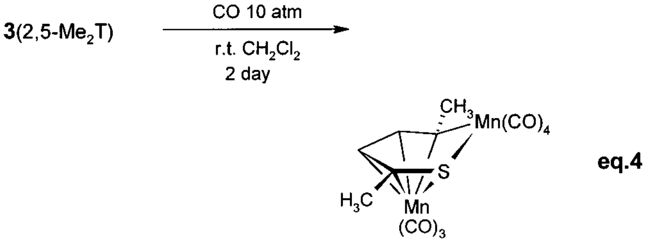
2

3

3(T) (R^1=R^2=R^3=H)
3(2-MeT) (R^1=Me, R^2=R^3=H)
3(3-MeT) (R^1=R^2=H, R^3=Me)
3(2,5-Me$_2$T) (R^1=R^2=Me, R^3=H)

The C−S bond cleavage and Mn(CO)$_n$ insertion in eq 3 is similar to that between [(benzothiophene)Ru(C$_6$Me$_6$)]$^{2+}$ and [(C$_{10}$H$_8$)Mn(CO)$_3$]BF$_4$ in the presence of Cp$_2$Co.[11] However, there are significant differences. Starting from a mononuclear complex, the ring-opened thiophene in **3** spans three metals via sulfur and carbon atoms. Mononuclear metal complexes that activate thiophene via formation of a dinuclear are already known. These compounds can serve as good models for intermediates in the HDS reaction. As far as we are aware, **3** is the first trinuclear complex with ring-opened thiophenes and with two metal−metal bonds. There have been several reports on μ_3-bound complexes, some of which are η^4,S-μ_3-bound thiophene complexes that are prepared from the reaction of a η^4-thiophene complex with dinuclear complexes.[1b,12] This observation may relate to the binding modes of sulfur-containing hydrocarbons to a metal-sulfide surface, intermediates in the HDS reaction, and homogeneous reactions containing a promoter. Examples of desulfurization of thiophenes by polynuclear complexes have been reported by Curtis,[13] Angelici,[14] Rauchfuss,[15] Jones,[16] Suzuki,[17] and Bianchini.[18]

Treatment of **3**(2,5-Me$_2$T) with 10 atm of CO led to the isolation of **7**(2,5-Me$_2$T) (eq 4), which was reported previously by Sweigart et al.[4a]



7(2,5-Me$_2$T)

During this carbonylation reaction, the ruthenium segment was removed, the Mn−Mn bond was cleaved, and the bonding mode of manganese metal changed from η^3 to η^5. This result suggests that under catalytic conditions the bonding mode of thiophenic is variable.

Reaction between [(selenophene)Ru(C$_6$Me$_6$)]$^{2+}$ (8) and 2 in the Presence of Cp$_2$Co. Selenophene and thiophene are related compounds, and we decided to investigate whether the C−Se bond of selenophene complex (selenophene)Ru(C$_6$Me$_6$)$^{2+}$ (**8**) could be cleaved in the same way as the C−S bond of **3** was cleaved.

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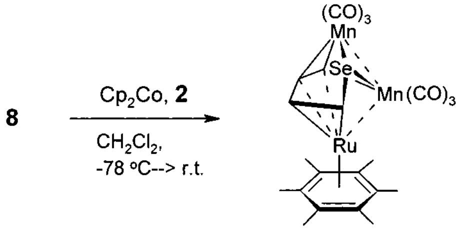
Table 1. Crystal Data and Structure Refinement for 3(T) and 9

	3(T)	**9**
chem formula	$C_{22}H_{22}Mn_2O_6RuS$	$C_{22}H_{22}Mn_2O_6RuSe$
fw	625.41	672.31
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a, Å	12.1761(6)	9.1816(13)
b, Å	9.1295(6)	11.0230(2)
c, Å	20.9970(2)	12.5487(8)
α, deg	90	75.081(9)
β, deg	97.965(5)	82.953(9)
γ, deg	90	68.606(12)
V, Å^3	2312.1(3)	1142.1(2)
Z	4	2
density calc, g cm^{-3}	1.788	1.955
θ range	1.69−24.98	1.68−24.97
no. of data	4047	4001
no. of params	311	311
R (all data)	0.0305	0.0484
wR_2 (all data)	0.0638	0.1248

Compound **8** was synthesized in the same way as **1**. Treatment of **8** in CH_2Cl_2 with Cp_2Co and **2** at −78 °C led to the isolation of the C−Se cleaved $RuMn_2$ complex **9** (eq 5) in 34% yield.



eq.5

9

It has been reported[19] that the trinuclear carbonyl clusters $[Os_3(CO)_{12-n}(CH_3CN)_n]$ (n = 0−2), $M_3(CO)_{12}$ (M = Fe, Ru) react with selenophene and tellurophene under mild conditions to give compounds containing the open-chain ligands CHCHCHCHX (X = Se, Te) or the fragments X, C_4H_4, C_4H_3, or H as bridging ligands.

X-ray Crystal Structures of 3(T) and 9. The X-ray crystal structure of **3**(T) is presented in Figure 1. The crystal structure of **9** is essentially the same as that of **3**(T), except for the presence of selenium instead of sulfur. An ORTEP drawing of **9** is available in the Supporting Information. Crystal and refinement data are given in Table 1, and selected bond distances and angles are listed in Table 2.

The three metals in **3**(T) are directly bonded to the ring-cleaved thiophene with η^4-, η^3-, and η^2-bonding modes. The Mn−Mn bond length in **3**(T) is 2.6715(6) Å, which is close to the value of 2.673(1) Å found for $Mn_2(CO)_7[\mu\text{-}\eta^4\text{-}C_3H_3NEt_2]$.[20] The Ru−Mn bond length of 2.7997(4) Å is comparable to the 2.7937(8) Å distance found for $[PPN][MnRu_3(CO)_{12}(\eta^2\text{-}\mu_3\text{-}NC(\mu\text{-}O)CH_3)$.[21] The sulfur folds up out of the four-carbon plane at a distance of 3.339 Å from the Ru, which is longer than 2.859(1) Å in $(\eta^5\text{-}Me_4C_4S)Ru\{\eta^4{:}\eta^1\text{-}Me_4C_4S\ (Fe(CO)_4)\}$.[22] For the $\eta^4{:}\eta^1\text{-}H_4C_4S$ ligand, the S atom is bent out of the diene-like plane with a dihedral angle (between C1−C2−C3−C4−Mn and Mn(1)−S−C(1)) of 66.8° for **3**(T). The atoms of Mn(1), C(4), C(3), C(2), and C(1) roughly define a plane. The hexamethylbenzene ring and the diene portion of the $\eta^4{:}\eta^1\text{-}H_4C_4S$ are mutually parallel with a dihedral angle of only 7.1° for **3**(T). The Mn(1)−C(4) bond distance (2.005(3) Å for **3**(T)) is quite close to the 2.009 Å bond distance of Mn−C(vinyl) in *trans*-1,2-$\{Mn(CO)_4[C,S\text{-}C(CO_2Cy){=}(CO_2Cy)S]\}_2C_2(C_6H_4F\text{-}p)_2$.[23] The Mn(2)−C(4) bond distance (2.128(2) Å for **3**(T)) is close to the value of 2.134 Å of Mn−C (1,3-butadienyl).[24]

Conclusion

Trimetallic compounds containing C−S cleaved thiophene were obtained when $(thiophene)Ru(C_6Me_6)^{2+}$ was reacted with $[(1\text{-methylnaphthalene})Mn(CO)_3]BF_4$ in the presence of Cp_2Co. Since HDS catalyst surfaces are multimetallic, it follows that one metal could activate the thiophene substrate by π-coordination, making it easier for a second metal to insert into a C−S bond. Reactions discussed in this paper may be relevant to the reactions on HDS catalyst surfaces and may provide evidence for and lead to a model for the strong activation of thiophene on multimetallic sites. The generality of the new C−X (X = S and Se) bond cleavage reaction of thiophene or selenophene complexes for other transition metals is currently under investigation.

Experimental Section

General Information. All solvents were carefully dried by conventional methods prior to use,[25] and all synthetic procedures were done under nitrogen atmosphere. Reagent grade chemicals were used without further purification.

Elemental analyses were done at the Inter-University Center for Natural Science Facilities, Seoul National University. ^1H NMR spectra were obtained with a Bruker DPX-300 instrument. Infrared spectra were recorded on a Shimadzu IR 470 spectrometer. Compounds **1** and **2** were prepared by the known procedures.[26,27]

Reaction of 1 with 2 and Cp₂Co. A typical reaction procedure is as follows: **1**(2,5-Me_2T) (0.156 g, 0.23 mmol) and **2** (0.195 g, 0.53 mmol) were dissolved in 15 mL of CH_2Cl_2 and cooled to −78 °C. To the solution was added Cp_2Co (0.110 g, 0.58 mmol). The resulting solution was stirred at −78 °C for 2 h and allowed to warm to room temperature. Filtration, concentration, and chromatography on a silica gel column (1.5 × 15 cm) eluting with CH_2Cl_2 and hexane (v/v, 1:1) gave **3**(2,5-Me_2T) in 24% yield (29 mg). ^1H NMR (acetone-d_6): δ 5.46 (d, 4.5 Hz, 1 H), 3.16 (s, 3 H, CH_3), 2.97 (d, 4.5 Hz, 1 H), 2.34 (s, 18 H, C_6Me_6), 1.41 (s, 3 H, CH_3) ppm. IR (CH_2Cl_2): ν_{CO} 2005 (m), 1962 (vs), 1911 (s) cm^{-1}. Anal. Calcd for $C_{24}H_{26}Mn_2O_6RuS$: C, 44.11; H, 4.01. Found: C, 44.02; H, 4.01.

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Table 2. Elected Bond Distances (Å) and Angles (deg) for 3(T) and 9

			3(T)		
Ru−Cl	2.198(3)	Ru−C2	2.105(3)	Ru−C3	2.194(2)
Ru−C4	2.166(2)	Ru−C10	2.252(2)	Ru−Mn1	2.7997(4)
Mn1−C4	2.005(3)	Mn1−S	2.3165(7)	Mn1−Mn2	2.6715(6)
Mn2−S	2.3003(7)	Mn2−C3	2.352(3)	Mn2−C4	2.128(2)
Mn1−S−Mn2	70.71(2)	Mn2−Mn1−Ru	88.66(2)	Mn2−S−Cl	100.51(9)
Mn2−Mn1−C4	51.77(7)	Mn1−C4−C3	129.2(2)	C2−C3−C4	121.8(2)
			9		
Mn2−Cl	1.994(4)	Mn2−Se	2.4372(8)	Mn1−Mn2	2.714(10)
Mn2−Se	2.4261(8)	Mn1−C1	2.095(4)	Mn1−C2	2.312(4)
Ru−Cl	2.157(4)	Ru−C2	2.187(4)	Ru−C3	2.109(4)
Ru−C4	2.193(4)	Ru−C5	2.218(4)	Ru−Mn2	2.8130(8)
Mn1−Se−Mn2	67.85(2)	Mn1−Mn2−Ru	87.34(3)	Mn1−Se−C4	95.67(14)
Mn1−Mn2−C1	50.03(12)	Mn2−C1−C2	130.3(3)	C1−C2−C3	121.9(4)

Analytical Data for 3(2-MeT). Yield: 21%. ^{1}H NMR (acetone-d_6): δ 9.75 (d, 6.7 Hz, 1 H, H^1), 5.60 (d, 4.5 Hz, 1 H, H^3), 2.96 (dd, 4.5, 6.7 Hz, 1 H, H^2), 2.35 (s, 18 H, $C_6\mathit{Me}_6$), 1.42 (s, 3 H, CH_3) ppm. IR (CH_2Cl_2): ν_{CO} 2005 (m), 1960 (vs), 1904 (s) cm^{-1}. Anal. Calcd for $C_{23}H_{24}Mn_2O_6RuS$: C, 43.20; H, 3.78; S, 5.01. Found: C, 42.79; H, 3.47; S, 5.16.

Analytical Data for 3(3-MeT). Yield: 22%. ^{1}H NMR (acetone-d_6): δ 9.52 (d, 6.7 Hz, 1 H, H^1), 3.15 (dd, 1.1, 6.7 Hz, 1 H, H^2), 2.35 (s, 18 H, $C_6\mathit{Me}_6$), 1.98 (s, 3 H, CH_3), 1.92 (d, 1.1 Hz, 1 H, H^4) ppm. IR (CH_2Cl_2): ν_{CO} 2005 (m), 1962 (vs), 1911 (s) cm^{-1}. Anal. Calcd for $C_{23}H_{24}Mn_2O_6RuS$: C, 43.20; H, 3.78; S, 5.01. Found: C, 42.87; H, 3.47; S, 5.18.

Analytical Data for 3(T). Yield: 22%. ^{1}H NMR (acetone-d_6): δ 9.59 (d, 6.8 Hz, 1 H, H^1), 5.44 (dd, 4.5, 5.1 1 H, H^3), 3.34 (ddd, 1.1, 4.5, 6.8 Hz, 1 H, H^2), 2.37 (s, 18 H, $C_6\mathit{Me}_6$), 2.27 (dd, 1.1, 5.1 Hz, 1 H, H^4) ppm. IR (CH_2Cl_2): ν_{CO} 2005 (m), 1962 (vs), 1911 (s) cm^{-1}. Anal. Calcd for $C_{22}H_{22}Mn_2O_6RuS$: C, 42.25; H, 3.55. Found: C, 42.17; H, 3.58.

Synthesis of 8. Under an atmosphere of nitrogen, 0.15 g of AgOTf (0.59 mmol) was added to an orange slurry of 0.10 g of $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ (0.15 mmol) in 20 mL of CH_2Cl_2. After the solution was stirred for 2 h, the solution was filtered. To the deep red filtrate was added 0.1 mL of selenophene. After the solution was stirred for 12 h, the light yellow solid was collected by filtration and washed with diethyl ether (20 mL) and pentane (20 mL). Yield: 0.19 g (93%). ^{1}H NMR (acetone-d_6): δ 7.68 (m, 2 H), 7.32 (m, 2 H), 2.70 (s, 18 H) ppm. Anal. Calcd $C_{18}H_{22}F_6O_6RuS_2Se$: C, 31.22; H, 3.20. Found: C, 31.05; H, 2.80.

Reaction of 8 with 2 and Cp$_2$Co. The same procedure as the synthesis of **3** was applied except **8** was used instead of **1**. Yield: 34%. IR (CH_2Cl_2): ν_{CO} 2005 (m), 1962 (vs), 1910 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 9.98 (d, 6.9 Hz, 1 H), 5.54 (t, 5.1 Hz, 1 H), 3.44 (t, 5.7 Hz, 1 H), 2.36 (s, 18 H), 2.26 (d, 5.5 Hz, 1 H) ppm. Anal. Calcd for $C_{22}H_{22}Mn_2O_6RuSe$: C, 39.33; H, 3.30. Found: C, 39.51; H, 3.36.

Carbonylation of 3(2,5-Me$_2$Th). A Teflon liner containing a solution of **3**(2,5-Me$_2$Th) (28 mg, 0.043 mmol) in 8 mL of CH_2Cl_2 was placed in a 100 mL autoclave equipped with a magnetic stirring bar. The autoclave was flushed with CO and then pressureized to 10 atm at room temperature. After the reaction mixture was stirred for 2 days, the excess CO was released, the solution was filtered, and the filtrate was concentrated and chromatographed on a silica gel column (1.5 × 15 cm) eluting with hexane. Removal of the solvent gave yellow solids **7** (6.1 mg, 34%). Single crystals of **7** suitable for an X-ray study were grown. ^{1}H NMR ($CDCl_3$): δ 6.59 (d, 5.5 Hz, 1 H, H^{2or3}), 5.37 (d, 5.5 Hz, 1 H, H^{2or3}), 2.47 (s, 3 H, CH_3), 2.20 (s, 3H, CH_3) ppm. IR (hexane): νCO 2079 (m), 2033 (vs), 1995 (vs), 1991 (s), 1969 (s), 1956 (s) cm^{-1}.

X-ray Structure Determination of 3(T) and 9. Crystals of **3**(T) and **9** were grown by slow evaporation of a solution of CH_2Cl_2 and pentane (v/v, 1:1) of **3**(T) and **9**, respectively. Diffraction experiments were performed by using an Enraf-Nonius CAD4 automated diffractometer with a $\omega-2\theta$ scan method. Unit cells were determined by centering 25 reflections in the appropriate 2θ range. Other relevant experimental details are listed in Table 1. The selected bond distances and angles are shown in Table 2. The structure was solved by direct methods with SHELXS-86 and refined by full-matrix least-squares with SHELXL-93. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined isotropically by using the riding model with 1.2 times the equivalent isotropic temperature factors of the atoms to which they are attached.

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Supporting Information Available: ORTEP drawings of **3**(T) and **9** and tables of atomic coordinates and equivalent isotropic parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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