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Trinuclear Rh_2M Complexes (M = Ni, Pd) Bridged by Butyl Selenolato and Carborane Diselenolato Ligands

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*Summary: Two new half-sandwich trinuclear Rh_2M (M = Ni, Pd) complexes bridged by butyl selenolato and carborane diselenolato ligands, $[Cp^*Rh\{\mu\text{-}Se_2C_2(B_{10}H_{10})\}]_2M[\mu\text{-}Se(C_4H_9)]_2$ [M = Ni (**4**), Pd (**5**)], have been prepared by the reactions of the $[Cp^*Rh\{\mu\text{-}Se_2C_2(B_{10}H_{10})\}\{\mu\text{-}Se(C_4H_9)\}]^-$ anion with $NiCl_2$ and $Pd(PhCN)_2Cl_2$, respectively. The complexes have been fully characterized by ^1H, ^{13}C, and ^{11}B NMR and IR spectroscopy as well as by element analyses. The molecular structures of **4** and **5** have been determined by single-crystal X-ray diffraction analyses, which show the central MSe_4 moiety in a slightly distorted square-planar coordination geometry for M = Ni, Pd.*

Introduction

The continuing intense interest in multinuclear transition metal complexes containing sulfur or selenium donor ligands is stimulated by their significant relevance to biological processes and their potential in solid state and catalytic applications.[1] This area of chemistry abounds with complexes of mono- and bidentate thiolates,[2] as well homo- or hetero-polynuclear complexes containing bridging *mono*thiolates (RS−),[3] *di*thiolate bridging ligands (−SRS−),[4] or *tri*dentate dithiolate-thioether ligands,[5] but heteronuclear complexes containing selenoether-selenolate ligands are rare.[6] On the other hand, the synthesis and study of organometallic complexes possessing an ancillary *o*-carborane dichalcogenolato ligand have continued to receive attention.[7] 1,2-Dicarba-*closo*-dodecaborane-1,2-dichalcogenolates (*ortho*-carborane dichalcogenolates) can be used as the voluminous and chemically robust chelate ligands to form half-sandwich complexes of the type $[Cp^*M\{E_2C_2(B_{10}H_{10})\}]$ ($Cp^* = \eta^5\text{-}C_5Me_5$, M = Co, Rh, Ir; E = S, Se), which can be used for further transformations in a controlled way under various conditions.[8−12] Owing to their rigid backbone, our recent studies have focused on the development of the rational methods to obtain the metal-chalcogenido cores with desired metal and chalcogen compositions. In this paper, we report the synthesis of the $[Cp^*Rh\{\mu\text{-}Se_2C_2(B_{10}H_{10})\}\{\mu\text{-}Se(C_4H_9)\}]^-$ anion as the metallaligand to react with transition metal compounds to afford the half-sandwich mixed-metal trinuclear complexes bridged by selenobutyl-diselenolatocarborane ligands.

Results and Discussion

Previously, we have reported that treatment of $[Cp^*Rh(\mu\text{-}Cl)Cl]_2$ with dilithium dichalcogenolato carboranes $Li_2E_2C_2(B_{10}H_{10})$ gave the 16-electron dichalcogenolate complexes $Cp^*Rh[E_2C_2(B_{10}H_{10})]$ (E = S (**1a**), Se (**1b**)) and investigated

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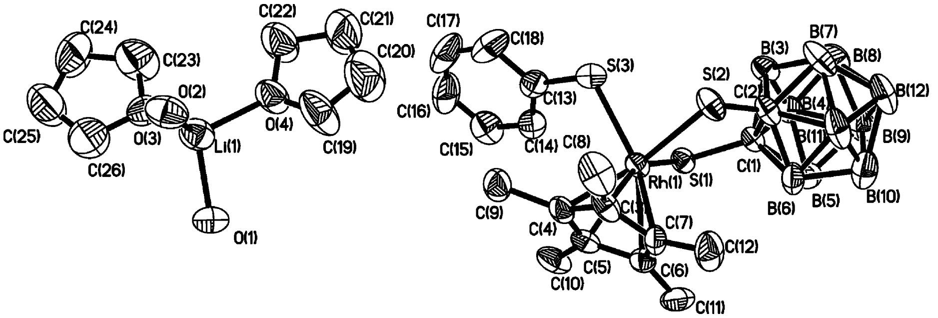
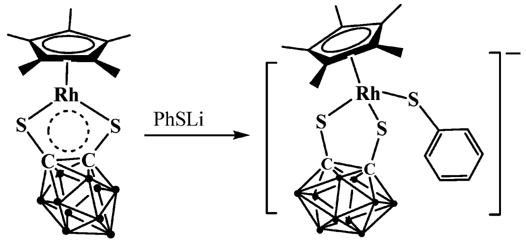


Figure 1. ORTEP drawing of **2**·[Li(THF)$_2$(H$_2$O)$_2$] (30% probability). Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Rh(1)−S(1), 2.375(3); Rh(1)−S(2), 2.357(3); Rh(1)−S(3), 2.380(3); C(1)−S(1), 1.775(9); C(2)−S(2), 1.780(10); C(1)−C(2), 1.671(13); C(13)−S(3), 1.764(13); S(1)−Rh(1)−S(2), 89.58(9); S(1)−Rh(1)−S(3), 92.02(10); S(2)−Rh(1)−S(3), 82.28(11); Rh(1)−S(3)−C(13), 112.6(4).

Scheme 1. Synthesis of Complex 2



1a **2**

the addition reactions at the rhodium atom.[9] The group 16 chalcogeno ether ligands ER$_2$ (E = S, Se, or Te) are usually regarded as modest σ-donors to transition metal centers;[7] the reaction of Cp*Rh[S$_2$C$_2$(B$_{10}$H$_{10}$)] (**1a**) with LiSPh could afford the lithium salt of Cp*Rh(μ-SPh)[S$_2$C$_2$(B$_{10}$H$_{10}$)]$^-$ (**2**) (Scheme 1).[13]

We attempted to synthesize multinuclear complexes using 1,2-dicarba-*closo*-dodecaborane-1,2-dithiolato and phenylthiolato ligands of complex **2** to hold two metal atoms in close proximity. The procedures failed when complex **2** was used as the starting material to react with NiCl$_2$ and Pd(PhCN)$_2$Cl$_2$, respectively, due to the intramolecular stereoelectronic influence of the phenylthiolato ligand and the high reactivity of the derivatives.

Complex **2** can be recrystallized from THF at low temperature to give well-formed red, single crystals in the triclinic space group $P\bar{1}$ with four molecules in the unit cell. The X-ray structure analysis of **2** confirms the ionic nature of the complex, and the molecular structure of [Cp*Rh(μ-SPh){S$_2$C$_2$(B$_{10}$H$_{10}$)}]·[Li(THF)$_2$(H$_2$O)$_2$] is shown in Figure 1. The anion structure of **2** shows a six-coordinate geometry about the rhodium atom, assuming that the Cp* ring serves as a three-coordinate ligand. The Rh−S distance (Rh(1)−S(1) 2.375(3) Å, Rh(1)−S(2) 2.357(3) Å) at the formally 18-electron metal center is significantly longer than that of the corresponding 16-electron complexes Cp′Rh[S$_2$C$_2$(B$_{10}$H$_{10}$)] (Cp′ = Cp*, η^5-1,3-^{t}Bu$_2$C$_5$H$_3$) (2.263 Å (av) for Cp*, 2.249 Å (av) for η^5-1,3-^{t}Bu$_2$C$_5$H$_3$),[9,12] which is due to p-orbital donation of the lone pairs from the sulfur atoms to the electron-deficient metal center. The rhodium atom environment is transferred from a two-legged piano-stool geometry in the 16-electron complex to a three-legged version in the 18-electron complex. The 16-electron pseudoaromatic metalladichalcogenolene heterocyclic system is destroyed and bent with a dihedral angle of 159.4° for compound **2**, along the S···S vector, which is due to the coordination of the SPh fragment to the metal center.

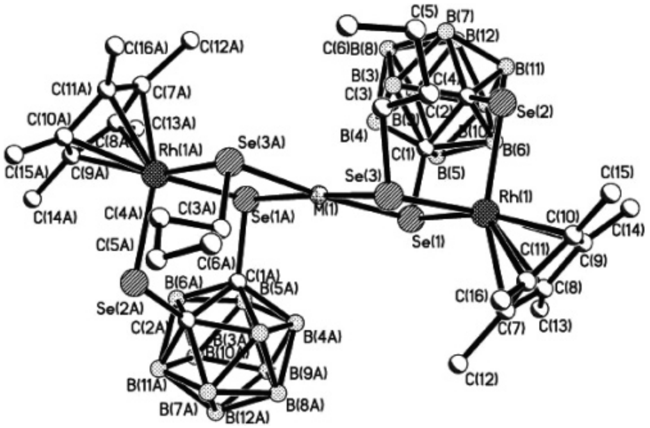


Figure 2. Molecular structures of **4** and **5** (30% probability). Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg) for **4** (M = Ni): Ni(1)−Se(1), 2.3727(11); Ni(1)−Se(3), 2.3119(11); Rh(1)−Se(3), 2.4459(10); Rh(1)−Se(1), 2.4562(9); Rh(1)−Se(2), 2.4643(11); Se(1)−C(1), 1.968(6); Se(2)−C(2), 1.924(7); Se(3)−C(13), 1.934(7); C(1)−C(2), 1.654(9); Se(3)−Ni(1)−Se(1), 85.04(3); Se(3)−Rh(1)−Se(1), 80.47(3); Se(3)−Rh(1)−Se(2), 94.26(3); Ni(1)−Se(1)−Rh(1), 96.10(4); Ni(1)−Se(3)−Rh(1), 97.99(4). Selected distances (Å) and angles (deg) for **5** (M = Pd): Pd(1)−Se(3), 2.4102(12); Pd(1)−Se(1), 2.4795(11); Rh(1)−Se(3), 2.4621(12); Rh(1)−Se(2), 2.4634(12); Rh(1)−Se(1), 2.4686(11); Se(1)−C(1), 1.955(7); Se(2)−C(2), 1.957(8); Se(3)−C(3), 1.918(8); C(1)−C(2), 1.627(9); Se(3)−Pd(1)−Se(1), 83.68(3); Se(3)−Rh(1)−Se(2), 94.28(4); Se(3)−Rh(1)−Se(1), 82.84(4); Se(2)−Rh(1)−Se(1), 91.57(4); Pd(1)−Se(1)−Rh(1), 95.63(4); Pd(1)−Se(3)−Rh(1), 97.61(5).

In order to gain stable, neutral multinuclear compounds, we prepared the voluminous substituted lithium salt of Cp*Rh(μ-Se^{n}Bu)[Se$_2$C$_2$(B$_{10}$H$_{10}$)]$^-$ (**3**), which was obtained from the reaction of **1b** with LiSe^{n}Bu. Furthermore, the anion complex **3** derived from selenobutyl-selenolatocarborane could be reacted with nickel or palladium[13] complexes to afford hetero-trinuclear complexes containing the (Rh$_2$M) cores (M = Ni, Pd) (Scheme 2).

Complexes **4** and **5** are moderately soluble in CH$_2$Cl$_2$ and THF, but only sparingly soluble in toluene and insoluble in *n*-hexane.

The structures of **4** and **5** have been determined by X-ray analyses using single crystals grown by slow diffusion of hexane into dichloromethane solution of the corresponding compounds, after chromatography on silica. Both of them are in the form of orange prisms in the monoclinic space group $C2/c$ with four molecules in the unit cell. The molecular structures and selected bond distances and angles of **4** and **5** are depicted in Figure 2.

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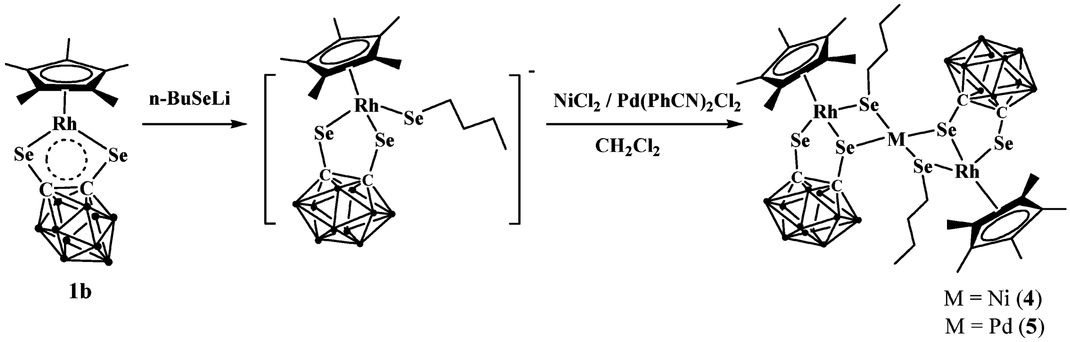
Scheme 2. Synthesis of Complexes 4 and 5



The ORTEP diagrams of **4** and **5** (Figure 2) show that the two complexes have similar structures. The heteronuclear complexes contain two *o*-carborane selenolato ligands, two butyl-selenolato ligands attached to the Cp*Rh fragment, and a nickel or palladium metal center. The Rh−Se distances are 2.4562(9) and 2.4643(11) Å for compound **4** and 2.4634(12) and 2.4686(11) Å for compound **5**, longer than that of a "pseudoaromatic" five-membered rhodadithiolene ring in Cp*Rh[$Se_2C_2(B_{10}H_{10})$] (2.3553 Å (av)).[9] The planar pseudoaromatic system of the two rhodadiselenene heterocycles **1b** is no longer present in **4** or **5**; the dihedral angle at the Se···Se vector in the $RhSe_2C_2$ ring is 160.5° for compound **4** and 162.3° for compound **5**. The M−Se(butyl) bond (2.3119(11) Å for **4** and 2.4102(12) Å for **5**) is distinctively shorter than the M−Se(carborane) bond (2.3727(11) Å for **4** and 2.4795(11) Å for **5**); the *cis* position of the butyl-selenolato ligand as the stronger bonded selenium donor is favored due to electronic reasons. The four-membered metallacycle Rh(1)Se(1)M(1)Se(3) is almost planar, the dihedral angle along the Se···Se vector being 173.5° for **4** and 174.9° for **5**. The dihedral angle of the plane M(1)-Se(1)Se(3) and the plane M(1)Se(1A)Se(3A) is 171.1° for **4** and 174.0° for **5** and the cis angles at the metal center are in the range 83.7−100.9°. Thus, the metal center lies perfectly on the square plane defined by the four donor atoms. The long Rh(1)···M(1) separation (3.592 Å for **4** and 3.666 Å for **5**) and the obtuse angle (M(1)−Se(1)−Rh(1) 96.10(4)° for **4** and 95.63(4)° for **5**, M(1)−Se(3)−Rh(1) 97.99(4)° for **4** and 97.61(5)°for **5**) indicate that a direct bonding interaction between the rhodium and metal center (nickel or palladium) is absent.

In summary, two new half-sandwich mixed-metal Rh_2M (M = Ni, Pd) trinuclear complexes bridged by selenobutyl-selenolatocarborane ligands, [Cp*Rh{μ-$Se_2C_2(B_{10}H_{10})$}]$_2$M[μ-$Se(C_4H_9)$]$_2$ [M = Ni (**4**), Pd (**5**)], have been prepared by reactions of the [Cp*Rh{μ-$Se_2C_2(B_{10}H_{10})$}{μ-$Se(C_4H_9)$}]$^-$ anion with $NiCl_2$ and $Pd(PhCN)_2Cl_2$, respectively. The molecular structures of **4** and **5** have been determined by X-ray crystallography. A detailed investigation on the reaction chemistry of heteronuclear complexes bridged by mixed alkyl chacogenolato and carborane chacogenolato ligands is under way.

Experimental Section

General Procedure. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. All solvents were dried and deoxygenated before use. The solvents THF, toluene, and *n*-hexane were refluxed and distilled over sodium/benzophenone ketyl under nitrogen prior to use. Silica gel, Merck 60 (0.06−0.2 mm), was activated at 400 °C and stored under nitrogen before use in chromatography. The starting materials [Cp*Rh{$E_2C_2(B_{10}H_{10})$}] [E = S (**1a**), Se (**1b**)], and $Pd(PhCN)_2Cl_2$[13] were prepared by literature procedures.

Elemental analyses were performed on an Elementar III Vario EI analyzer. NMR measurements were carried out using Bruker AC500 spectrometers (chemical shifts are given with respect to $CHCl_3/CDCl_3$ ($\delta^1H = 7.24$; $\delta^{13}C = 77.0$), external Et_2O-BF_3 ($\delta^{11}B = 0$ for $\Xi(^{11}B) = 32.08$ MHz)). Infrared spectra were obtained on a Nicolet FT-IR 360 spectrometer (KBr pellet).

Preparations of Cp*Rh(μ-SPh)[$S_2C_2(B_{10}H_{10})$]$^-$ (2). PhSH (12 mg, 0.11mmol) was dissolved in diethyl ether (15 mL) and lithiated by the addition of *n*-butyllithium (39 μL, 0.11 mmol). The mixture was stirred for 1 h at room temperature. Then a solution of [Cp*Rh{$S_2C_2(B_{10}H_{10})$}] (**1a**) (44 mg, 0.1 mmol) in THF (20 mL) was added at ambient temperature. The resulting solution was stirred for 16 h, the solvent was then removed under vacuum, and the residue was purified by recrystallization with THF at −28 °C. **2**·Li(THF)$_2$-(H_2O)$_2$: 65 mg, 88%. Anal. Calcd (%) for $C_{26}H_{50}B_{10}LiO_4RhS_3$: C 42.15, H 6.80. Found: C 41.83, H 6.73. ^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm): 1.56 (s, H_2O), 1.80 (s, Cp*), 1.85 (m, CH_2 of THF), 3.76 (m, CH_2O of THF), 7.01−7.26 (m, Ph).

Preparation of [Cp*Rh{$Se_2C_2(B_{10}H_{10})$}]$_2${Ni(SeC_4H_9)$_2$} (4). [Cp*Rh{$Se_2C_2(B_{10}H_{10})$}] (**1b**) (109 mg, 0.2 mmol) was added to BuSeLi (0.1mmol) in diethyl ether (20 mL), and the mixture was stirred for 3 h at room temperature. Then a solution of $NiCl_2$ (0.1 mmol) in CH_2Cl_2 (20 mL) was added at ambient temperature. The color of the resultant mixture gradually changed from green to red. After 12 h the solvents were removed under reduced pressure and the residue was chromatographed on silica gel (2.0 cm × 40.0 cm). Elution with CH_2Cl_2/hexane (1:1) gave an orange zone. Evaporation and crystallization from CH_2Cl_2/hexane afforded **4** as orange prismatic crystals (73 mg, 52%). Anal. Calcd (%) for $C_{32}H_{68}B_{20}Se_6Rh_2Ni$: C 27.31, H 4.87. Found: C 27.42, H 4.90. ^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm): 0.94 (m, 6H, *CH$_3$*), 1.41 (m, 4H, *CH$_2$*), 1.57 (m, 4H, *CH$_2$*), 1.72 (s, 30H, *Cp**), 2.77 (m, 4H, Se*CH$_2$*). ^{13}C NMR (500 MHz, $CDCl_3$, δ/ppm): 10.53 (C_5Me_5), 15.45 (CH_3), 23.01 (CH_2), 28.05 (CH_2), 75.92 ($SeCH_2$), 98.73 (C_5Me_5, d, J = 5.20). ^{11}B NMR (160 MHz, $CDCl_3$, δ/ppm): −2.09, −7.06, −11.32, −13.89. IR (KBr disk): ν 2955, 2920, 2845 cm^{-1} (C−H), ν = 2568 cm^{-1} (B−H).

Preparation of [Cp*Rh{$Se_2C_2(B_{10}H_{10})$}]$_2${Pd(SeC_4H_9)$_2$} (5). [Cp*Rh{$Se_2C_2(B_{10}H_{10})$}] (**1b**) (109 mg, 0.2 mmol) was added to BuSeLi (0.1mmol) in diethyl ether (20 mL), and the mixture was stirred for 3 h at room temperature. Then a solution of Pd-($PhCN)_2Cl_2$ (28 mg, 0.1 mmol) in CH_2Cl_2 (20 mL) was added at ambient temperature. The color of the resultant mixture gradually changed from green to red. After 12 h the solvents were removed under reduced pressure and the residue was chromatographed on silica gel (2.0 cm × 40.0 cm). Elution with CH_2Cl_2/hexane (1:1) gave an orange zone. Evaporation and crystallization from CH_2Cl_2/hexane afforded **5** as orange prismatic crystals (95 mg, 65%). Anal. Calcd (%) for $C_{32}H_{68}B_{20}Se_6Rh_2Pd$: C 26.41, H 4.71. Found: C 26.21, H 4.65. ^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm): 0.90 (m, 6H, *CH$_3$*), 1.26 (m, 4H, *CH$_2$*), 1.59 (m, 4H, *CH$_2$*), 1.85 (s, 30H, *Cp**), 2.82 (m, 4H, Se*CH$_2$*). ^{13}C NMR (500 MHz, $CDCl_3$, δ/ppm): 9.32 (C_5Me_5), 14.06 (CH_3), 22.61 (CH_2), 29.66 (CH_2), 69.79

(SeCH$_2$), 98.70 (C_5Me$_5$, d, $J = 5.10$). ^{11}B NMR (160 MHz, CDCl$_3$, δ/ppm): −2.32, −7.08, −13.43, −14.47. IR (KBr disk): ν 2954, 2922, 2854 cm^{-1} (C−H), $\nu = 2562$ cm^{-1} (B−H).

X-ray Crystal Structure Determination of 2, 4, and 5. Crystals of **2**, **4**, and **5** were sealed under nitrogen in Lindemann glass capillaries for X-ray structural analysis. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer using graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. During the intensity data collection, no significant decay was observed. The intensities were corrected for Lorentz−polarization effects and empirical absorption with the SADABS program.[14] The structures were solved by direct methods using the SHELXL-97 program.[15] All non-hydrogen atoms were found from the difference Fourier syntheses. The H atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms but were not included in the refinement. All calculations were performed using the Bruker Smart program. Crystal data for **2**: $C_{26}H_{50}B_{10}LiO_4Rh_2S_3$, fw = 740.79, triclinic, $P\bar{1}$, $a = 12.094(2)$ Å, $b = 12.297(2)$ Å, $c = 14.618(3)$ Å, $\alpha = 88.707(3)°$, $\beta = 73.950(3)°$, $\gamma = 79.967(3)°$, $V = 2056.5(7)$ Å^3, $Z = 2$, R1 = 0.0683 for 7178 ($I > 2\sigma(I)$), wR2 = 0.2165 (all data). Crystal data for **4**: fw = 1492.28, monoclinic, $C2/c$, $a = 11.488(3)$ Å, $b = 21.292(5)$ Å, $c = 23.703(6)$ Å, $\alpha = 90°$, $\beta = 100.899(4)°$, $\gamma = 90°$, $V = 5693(2)$Å^3, $Z = 4$, R1 = 0.0424 for 5575 ($I > 2\sigma(I)$), wR2 = 0.0923 (all data). Crystal data for **5**: fw = 1539.97, monoclinic, $C2/c$, $a = 11.421(3)$ Å, $b = 21.371(7)$ Å, $c = 24.034(6)$ Å, $\alpha = 90°$, $\beta = 101.274(4)°$, $\gamma = 90°$, $V = 5753(3)$ Å^3, $Z = 4$, R1 = 0.0384 for 5080 ($I > 2\sigma(I)$), wR2 = 0.0665 (all data).

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Supporting Information Available: X-ray crystallographic data for complexes **2**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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