Subsequent Hydride Substitution in (Arene)trihydridodiruthenium Complexes: Synthesis and Structure of Thiolato-Bridged Diruthenium Cations of the Type $[H_2(arene)_2Ru_2(p\text{-}X-C_6H_4-S)]^+$ and $[H(arene)_2Ru_2(p\text{-}X-C_6H_4-S)_2]^+$

Mathieu J.-L. Tschan,[a] Frédéric Chérioux,*[a,b] Bruno Therrien,[a] and Georg Süss-Fink[a]

Dedicated to Professor Jean-Marie Lehn on the occasion of his 65th birthday

Keywords: Ruthenium / Sulfur / Hydrides / Complexes / Cross-coupling

The cationic complexes $[HRu_2(\eta^6\text{-arene})_2\{\mu_2\text{-}(p\text{-}X\text{–}C_6H_4)\text{–}S\}_2]^+$ and $[H_2Ru_2(\eta^6\text{-arene})_2\{\mu_2\text{-}(p\text{-}X\text{–}C_6H_4)\text{–}S\}]^+$ (arene = 1,2,4,5-$Me_4C_6H_2$ or C_6Me_6; X = Br and Me) are accessible in good yields from p-X–C_6H_4–SH with $[H_3Ru_2(1,2,4,5\text{-}Me_4C_6H_2)_2][BF_4]$ and $[H_3Ru_2(C_6Me_6)_2][BF_4]$, respectively. The dibromo derivative $[HRu_2(C_6Me_6)_2(p\text{-}Br\text{–}C_6H_4\text{–}S)_2]^+$ is found to undergo double Suzuki coupling reactions with 3-thiophene boronic acid to give $[HRu_2(C_6Me_6)_2(p\text{-}C_4H_3S\text{–}C_6H_4\text{–}S)_2]^+$. This dibromo complex is a potential precursor for the insertion of dinuclear hydrido organometallic entities in the main chain of conjugated molecules.

Introduction

The field of π-conjugated molecules and polymers containing metal centers has attracted continuous attention over the past two decades because of their electronic, magnetic, or catalytic properties,[1−4] and more recently, for the development of sensors.[5,6] To the best of our knowledge, except for a very recent work by Kim et al. who synthesized a dinuclear organomolybdenum sulfide complex,[7] all relevant molecules are built around mononuclear building blocks that are coordinated with different types of organic ligands. Therefore, there are still challenges to develop versatile and selective strategies, with the view of creating new molecular designs and bridging ligands for the formation of oligomers and polymers which contain metal centers.

In recent studies,[8−10] we have shown that dinuclear dichloro complexes $[Ru(\eta^6\text{-arene})Cl_2]_2$ and $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$ react in ethanol with p-bromothiophenol to give the cationic complexes $[Ru_2(\eta^6\text{-arene})_2\{\mu_2\text{-}(p\text{-}Br-C_6H_4)-S\}_3]^+$ and $[Rh_2(\eta^5\text{-}C_5Me_5)_2\{\mu_2\text{-}(p\text{-}Br-C_6H_4)-S\}_3]^+$, respectively, which could be isolated as the chloride salts in quantitative yield. We have also synthesized the first star-shaped π-conjugated oligomers built around dinuclear organometallic complexes.[11] The presence of bromo functions at the periphery of $[Ru_2(\eta^6\text{-arene})_2\{\mu_2\text{-}(p\text{-}Br-C_6H_4)-S\}_3]^+$ and $[Rh_2(\eta^5\text{-}C_5Me_5)_2\{\mu_2\text{-}(p\text{-}Br-C_6H_4)-S\}_3]^+$ was judiciously exploited to insert thiophene derivatives by standard Suzuki cross-coupling reactions.[12] However, despite the successful synthesis of conjugated oligomers (i.e. coupling with monoboronic acids), we were unable to characterize the corresponding polymers (i.e. coupling with diboronic acids). This can be explained by a large degree of reticulation due to the presence of three bromine atoms in the starting complexes. Consequently, the challenge consists of finding new complexes that contain only one or two bromine atoms (instead of three) at their periphery, therefore allowing a better control for the synthesis of conjugated polymers.

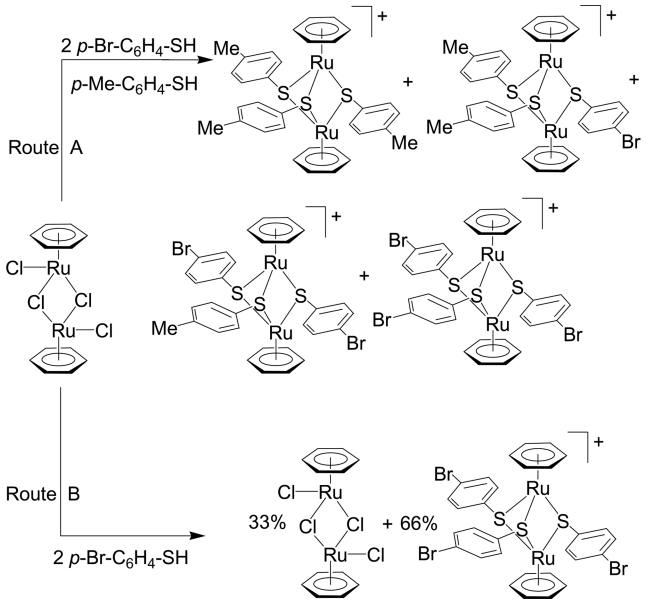
In this paper, we report the first example of dinuclear organometallic conjugated molecules in a "zig-zag"-like arrangement with mono- and disulfur connectivities, $[H_2Ru_2(\eta^6\text{-arene})_2\{\mu_2\text{-}(p\text{-}X-C_6H_4)-S\}]^+$ and $[HRu_2(\eta^6\text{-arene})_2\{\mu_2\text{-}(p\text{-}X-C_6H_4)-S\}_2]^+$, respectively, and give one example of extending their conjugation by Suzuki cross-coupling reactions with 3-thiophene boronic acid.

Results and Discussion

In order to overcome the reticulation problem which arises as a result of the three bromine atoms at the periphery of dinuclear precursors, we first focussed our attention on two different strategies to synthesize mono- and difunctional dinuclear complexes (see Scheme 1): in route A, dif-

[a] Institut de Chimie, Université de Neuchâtel,
Avenue de Bellevaux, 51 2000, Switzerland
Fax: (internat.) +41-327-182-511
E-mail: frederic.cherioux@unine.ch
[b] Département LPMO, Institut FEMTO-ST, CNRS UMR 6174,
32 Avenue de l'Observatoire, 25044 Besançon cedex, France
Fax: (internat.) +33-381-853-998
E-mail: frederic.cherioux@lpmo.edu

ferent *para*-substituted thiophenols are mixed together, leading to a mixture of all possible substitution compounds in a stoichiometric ratio, as observed by NMR (^{1}H and ^{13}C{^{1}H}) and mass spectrometry. In route B, an excess of the dinuclear dichloro complex is used to favor the formation of mono- and di-μ_2-thiolato complexes.

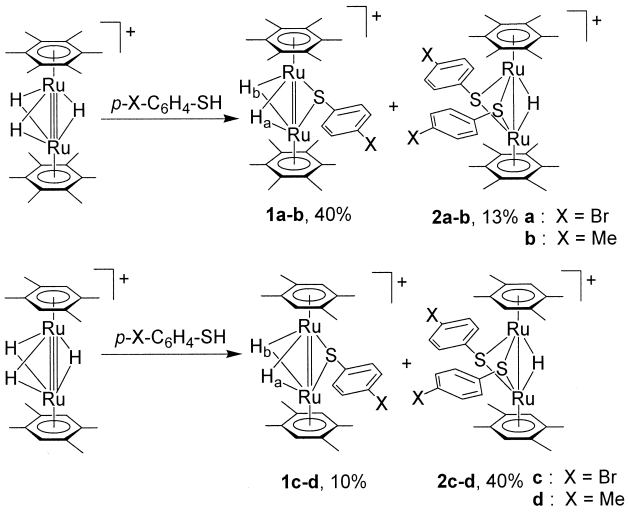


Scheme 1. Strategies for the synthesis of mono- or difunctional dinuclear complexes

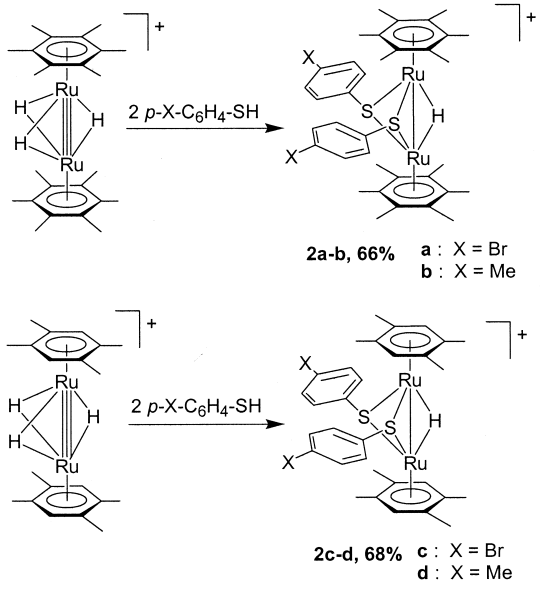
Unfortunately, the different compounds obtained as a mixture from route A could not be separated by standard chromatographic techniques, whereas route B only afforded tri-μ_2-thiolato complexes, despite a strict 1:2 ratio of the reagents.

Consequently, we reasoned that strategy B would, in principle, be the most promising method to synthesize of difunctional dinuclear complexes; however, the dinuclear dichloro complexes [Ru(η^6-arene)Cl$_2$]$_2$ were too reactive to stop at the formation of the di-μ_2-thiolato derivatives. In order to overcome this problem, we used the trihydrido complexes [H$_3$Ru$_2$(η^6-arene)$_2$]$^+$, which are accessible from the reaction of the dinuclear dichloro complexes [Ru(η^6-arene)Cl$_2$]$_2$ (arene: C$_6$Me$_6$, 1,2,4,5-Me$_4$C$_6$H$_2$) with NaBH$_4$,[13−15] instead of the dichloro complexes themselves.

The dinuclear trihydrido complex [H$_3$Ru$_2$(C$_6$Me$_6$)$_2$]$^+$ was found to react with one equivalent of *p*-X−C$_6$H$_4$−SH (X = Me or Br) in ethanol to give a mixture of the cationic complexes [H$_2$Ru$_2$(C$_6$Me$_6$)$_2$(*p*-X−C$_6$H$_4$−S)]$^+$ (**1a**−**b**) and [HRu$_2$(C$_6$Me$_6$)$_2$(*p*-X−C$_6$H$_4$−S)$_2$]$^+$ (**2a**−**b**) in a 3:1 ratio. These cationic complexes can be isolated in good yields as the tetrafluoroborate salts. In the case of the durene analogue [H$_3$Ru$_2$(1,2,4,5-Me$_4$C$_6$H$_2$)$_2$]$^+$, the reaction with one equivalent of *p*-X−C$_6$H$_4$−SH (X = Me or Br) in ethanol yields the cationic complexes [H$_2$Ru$_2$(1,2,4,5-Me$_4$C$_6$H$_2$)$_2$(*p*-X−C$_6$H$_4$−S)]$^+$ (**1c**−**d**) and [HRu$_2$(1,2,4,5-Me$_4$C$_6$H$_2$)$_2$(*p*-X−C$_6$H$_4$−S)$_2$]$^+$ (**2c**−**d**), in a 1:4 ratio (see Scheme 2).



Scheme 2. Reaction of [H$_3$Ru$_2$(η^6-arene)$_2$]$^+$ with one equivalent of *para*-substituted thiophenol



Scheme 3. Reaction of [H$_3$Ru$_2$(η^6-arene)$_2$]$^+$ with two or more equivalents of *para*-substituted thiophenol

Surprisingly, if two (or more) equivalents of *p*-X−C$_6$H$_4$−SH were used with [H$_3$Ru$_2$(η^6-arene)$_2$][BF$_4$], the reaction led exclusively to the formation of the cationic complexes [HRu$_2$(C$_6$Me$_6$)$_2$(*p*-X−C$_6$H$_4$−S)$_2$]$^+$ (**2a**−**b**) and [HRu$_2$(1,2,4,5-Me$_4$C$_6$H$_2$)$_2$(*p*-X−C$_6$H$_4$−S)$_2$]$^+$ (**2c**−**d**, see Scheme 3), and no trace of the mono- or tri-μ_2-thiolato complexes was detected by mass spectrometry.

Both cations **1** and **2** were unambiguously characterized as the tetrafluoroborate salts (see Exp. Sect.). These ionic compounds are highly soluble in alcohols, acetone and chlorinated solvents. The molecular structures of selected complexes **1a**, **2a**, **2c** and **2d** were confirmed by single-crystal X-ray structure analysis of the tetrafluoroborate salts. These cationic species consist of a trigonal bipyramidal

H_2Ru_2S or HRu_2S_2 core, each ruthenium atom being coordinated to an η^6-C_6Me_6 or an η^6-1,2,4,5-$Me_4C_6H_2$ ligand, and each sulfur atom carrying a *p*-substituted phenyl group. The molecular structures of **1a** and **2a** are shown in Figure 1, and those of **2c** and **2d** are shown in Figure 2.

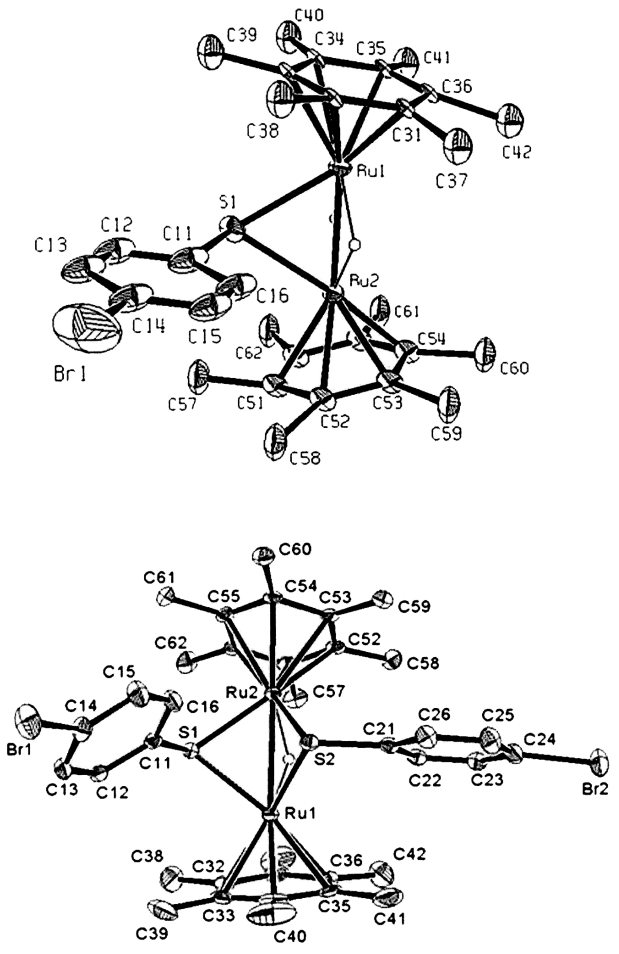


Figure 1. Molecular structures of [**1a**][BF_4] (top) and [**2a**][BF_4] (bottom); tetrafluoroborate anions, solvent molecules and H atoms have been omitted for clarity; displacement ellipsoids are drawn at the 25 and 35% probability level, respectively; selected bond lengths (Å) and angles (°) are listed in Table 1

The metal backbone of **1a** and **2a** consists of two ruthenium atoms, the Ru−Ru distances being in accordance with a metal−metal double bond [**1a**: Ru−Ru = 2.624(2) Å] or single bond [**2a**: Ru−Ru = 2.8112(6) Å]. The presence of one or two thiolato bridging ligands forces the arene−Ru−Ru−arene moieties to adopt a distorted geometry. The two C_6Me_6 arene ligands are not parallel to each other, and the angles between the C_6Me_6 planes are 21.2° in **1a** and 37.4° in **2a**.

The single-crystal X-ray structure analysis of [**1a**]BF_4 explains the large difference in the chemical shifts observed in ^{1}H NMR spectrum of this complex between the two hydrido ligands (−12.88 and −16.75 ppm), as well as that observed for the other dihydrido complexes **1b**−**d** (see Exp. Sect.). The angle defined by the μ_2-(*p*-X−C_6H_4)−S bridging ligand and the ruthenium atoms is close to 110°, thus

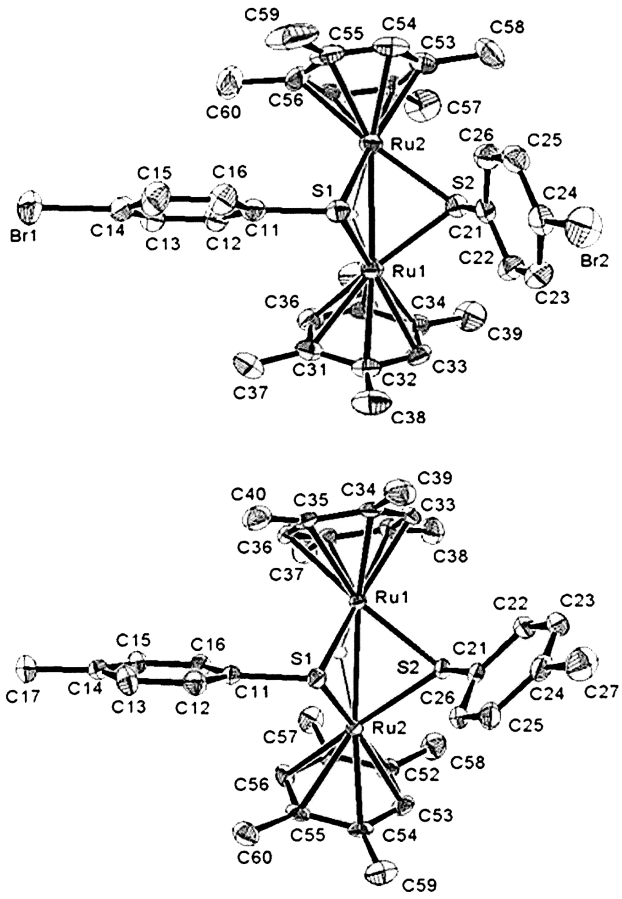


Figure 2. Molecular structures of [**2c**][BF_4] (top) and [**2d**][BF_4] (bottom); tetrafluoroborate anions and H atoms have been omitted for clarity; displacement ellipsoids are drawn at the 35 and 50% probability level, respectively; selected bond lengths (Å) and angles (°) are listed in Table 1

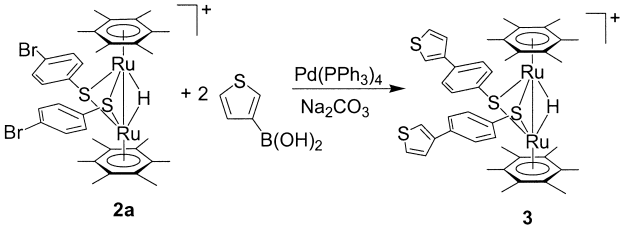
leading to a strongly distorted structure. Consequently, the two hydrido ligands are nonequivalent, because one of them, H_a (see Scheme 2), is closer to the *p*-X−C_6H_4−S moiety than the other (H_b). Moreover, H_a is in the plane of deshielding of the *para*-substituted thiophenyl group (see Figure 1). This phenomenon leads to a large difference in the chemical shift of H_a (−12.88 ppm) and H_b (−16.75 ppm), as observed in ^{1}H NMR spectrum of **1a**. As far as complexes **2** are concerned, the chemical shifts assigned to the hydrido ligands are found between −11 and −12 ppm. As the molecular structures of **2a**, **2c** and **2d** (see Figure 1 and Figure 2) reveal, the hydrido ligand of these complexes is also in the plane of deshielding of the thiophenyl moiety, leading to chemical shifts similar to those observed for the most deshielded hydrido ligands in complexes **1**.

The reactivities of the dinuclear trihydrido complexes $[H_3Ru_2(\eta^6\text{-arene})_2]^+$ are completely different from that of the $[Ru(\eta^6\text{-arene})Cl_2]_2$ complexes. In the case of the chloro-bridged complexes, only the trisubstituted products are formed, whereas the hydrido-bridged complexes exclusively give rise to mono- and dithiolato derivatives. This is probably due to the lower reactivity of the μ_2-hydrido ligand, relative to that of the μ_2-chloro ligand, which implies no

modification of the metal−metal bond during the replacement with a μ_2-thiolato ligand, as is the case for the substitution of a μ_2-hydrido bridge.

As only the disubstituted complexes $[HRu_2(\eta^6\text{-arene})_2\{\mu_2\text{-}(p\text{-}X{-}C_6H_4){-}S\}_2]^+$ (**2**) are accessible from the reaction of $[H_3Ru_2(\eta^6\text{-arene})_2]^+$ or $[H_2Ru_2(\eta^6\text{-arene})_2\{\mu_2\text{-}(p\text{-}X{-}C_6H_4){-}S\}_2]^+$ (**1**) with an excess of $p\text{-}X{-}C_6H_4{-}SH$, the introduction of a third *para*-substituted thiophenyl group seems impossible. In fact, the molecular structures of **2a**, **2c** and **2d** show an important constraint on the two arene ligands due to steric repulsion with the *para*-substituted thiophenyl groups already incorporated (see Figure 1 and Figure 2, selected bond lengths and angles are listed in Table 1), which prevents substitution of the last hydrido ligand by a third thiolato ligand. In addition, the steric hindrance provided by the arene moieties also controls the reactivity of $[H_3Ru_2(\eta^6\text{-arene})_2]^+$ with one equivalent of the *para*-substituted thiophenol. In this case, the ratio of complexes **1** and **2** formed is reversed by making the arene ligands more bulky: 1:4 for $1,2,4,5\text{-}Me_4C_6H_2$ in contrast to 3:1 for C_6Me_6 (see Scheme 1). Similar effects of arene ligands have not been observed so far in the case of $[Ru(\eta^6\text{-arene})Cl_2]_2$ complexes.[10,11] As a consequence, it can be stated that: i) $[Ru(\eta^6\text{-arene})Cl_2]_2$ complexes give only trisubstituted compounds ($[Ru_2(\eta^6\text{-arene})_2\{\mu_2\text{-}(p\text{-}X{-}C_6H_4){-}S\}_3]^+$), while the lower reactivity of $[H_3Ru_2(\eta^6\text{-arene})_2]^+$ leads to the mono- and disubstituted compounds, $[HRu_2(C_6Me_6)_2(p\text{-}X{-}C_6H_4{-}S)_2]^+$ and $[H_2Ru_2(C_6Me_6)_2(p\text{-}X{-}C_6H_4{-}S)]^+$; ii) the ratio between mono- and disubstituted complexes can be tuned by the steric hindrance of the arene substituents in the starting trihydrido complexes. This can be used for the synthesis of multifunctional complexes containing the desired number of functionalized ligands at the periphery.

In order to develop well-defined conjugated polymers possessing dinuclear organometallic entities, we investigated the ability of complex **2a** (substituted by two bromine atoms at its periphery) to react with boronic acid by a Suzuki cross-coupling reaction, as depicted in Scheme 3.



2a 3

Scheme 4. Suzuki cross-coupling reaction of 3-thiophene boronic acid with dibromo complex **2a**

Cation **2a** was found to react with 3-thiophene boronic acid in ethanol in the presence of $Pd(PPh_3)_4$ as a catalyst to give the conjugated complex $[HRu_2(C_6Me_6)_2(p\text{-}C_4H_3S{-}C_6H_4{-}S)_2]^+$ (**3**) with yields ranging from 10 to 15%. We observed the formation of the difunctionalized compounds only. Cation **3** was unambiguously characterized by standard methods (See Experimental Section). This cationic complex, as the tetrafluoroborate salt, is highly soluble in alcohols, acetone and chlorinated solvents. The molecular structure of **3** was confirmed by a single-crystal X-ray structure analysis of the BF_4 salt: the cation maintains the trigonal-bipyramidal HRu_2S_2 framework of its precursor, as shown in Figure 3.

New materials with unique properties should be accessible by this method, because standard organic dibromo reagents (for example 2,5-dibromothiophene, 2,7-dibromofluorene etc.) can be replaced by these organometallic entities. This original approach could lead to the development of

Table 1. Selected bond lengths (Å) and angles (°) for [**1a**][BF_4], [**2a**][BF_4], [**2c**][BF_4], [**2d**][BF_4], and [**3**][BF_4]

	[**1a**][BF_4]	[**2a**][BF_4]	[**2c**][BF_4]	[**2d**][BF_4]	[**3**][BF_4]
Interatomic distances					
Ru(1)−S(1)	2.420(9)	2.3642(10)	2.3740(11)	2.3635(8)	2.369(3)
Ru(1)−S(2)		2.3669(10)	2.3578(12)	2.3676(9)	2.340(3)
Ru(2)−S(1)	2.440(8)	2.3426(10)	2.3724(11)	2.3577(7)	2.374(3)
Ru(2)−S(2)		2.3744(10)	2.3594(11)	2.3548(7)	2.396(3)
Ru(1)−Ru(2)	2.624(2)	2.8112(6)	2.7845(5)	2.7963(5)	2.7884(12)
S(1)−C(11)	2.06(2)	1.787(4)	1.783(4)	1.794(3)	1.806(12)
S(2)−C(21)		1.779(4)	1.789(4)	1.789(3)	1.785(11)
C(14)−Br(1)	1.67(2)	1.894(4)	1.899(5)		
C(24)−Br(2)		1.904(4)	1.905(5)		
C(14)−C(17)				1.507(4)	1.441(15)
C(24)−C(27)				1.514(4)	1.516(15)
Angles					
Ru(1)−S(1)−Ru(2)	65.35(14)	73.35(3)	71.84(3)	72.64(2)	72.01(8)
Ru(1)−S(2)−Ru(2)		72.73(3)	72.35(3)	72.62(2)	72.13(9)
Ru(1)−S(1)−C(11)	110.9(7)	113.86(12)	112.33(15)	108.59(10)	111.5(3)
Ru(1)−S(2)−C(21)		108.17(13)	110.48(14)	108.12(10)	113.9(4)
Ru(2)−S(1)−C(11)	112.4(7)	116.34(12)	110.17(14)	109.87(9)	113.9(4)
Ru(2)−S(2)−C(21)		109.43(14)	111.67(14)	117.52(9)	117.0(4)

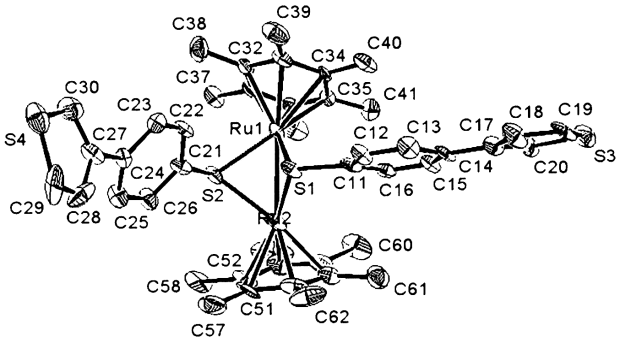


Figure 3. Molecular structure of [**3**][BF_4]; the tetrafluoroborate anion, solvent molecule, and H atoms have been omitted for clarity; displacement ellipsoids are drawn at the 25% probability level; selected bond lengths (Å) and angles (°) are listed in Table 1

promising materials based on the "zig-zag" design as a result of the disulfur connectivities of the type observed in $[HRu_2(C_6Me_6)_2(p\text{-}Br{-}C_6H_4{-}S)_2][BF_4]$.

Conclusion

In conclusion, we reported the synthesis of dinuclear organometallic entities, based on trigonal-bipyramidal HRu_2S_2 and H_2Ru_2S frameworks. We demonstrated that it is possible to control the functionalization (i.e. insertion of one or two *para*-substituted thiophenyl ligands) by the use of dinuclear trihydrido complexes $[H_3Ru_2(\eta^6\text{-arene})_2]^+$. The dibromo-substituted derivative $[HRu_2(C_6Me_6)_2(p\text{-}Br{-}C_6H_4{-}S)_2]^+$ reacts with 3-thiophene boronic acid by Suzuki cross-couplings to form the conjugated complex $[HRu_2(C_6Me_6)_2(p\text{-}C_4H_3S{-}C_6H_4{-}S)_2]^+$. The development of original and promising conjugated polymers from the dinuclear complexes possessing two bromine substituents at their periphery is currently under investigation.

Experimental Section

General Remarks: All reactions were carried out under a nitrogen atmosphere, by using standard Schlenk techniques, and the solvents were degassed prior to use. The dinuclear trihydrido complexes $[H_3Ru_2(\eta^6\text{-arene})_2]^+$ (arene: C_6Me_6, 1,2,4,5-$Me_4C_6H_2$) were synthesized by previously described methods.[16−18] All other reagents were purchased (Fluka, Acros) and used as received. NMR spectra were recorded on a Varian−Gemini 200 BB instrument and referenced to the signals of the residual protons in the deuterated solvents. The mass spectra were recorded at the University of Fribourg (Switzerland) by Prof. Titus Jenny. Microanalyses were carried out by the Laboratory of Pharmaceutical Chemistry, University of Geneva (Switzerland).

Preparation of $[H_2Ru_2(C_6Me_6)_2(p\text{-}X{-}C_6H_4{-}S)][BF_4]$: The dinuclear trihydrido salt $[H_3Ru_2(C_6Me_6)_2][BF_4]$ (50 mg, 81 μmol) and *p*-bromothiophenol (19 mg, 101 μmol) or *p*-thiocresol (12.5 mg, 101 μmol) were dissolved in degassed technical grade ethanol (60 mL) and heated under reflux for 16 hours. After cooling to room temperature, the purple solution was filtered, and the solvent was evaporated to dryness under reduced pressure. The purple solid was washed with diethyl ether (3 × 20 mL), dissolved in dichloromethane, and isolated by preparative thin-layer chromatography on silica (eluent: acetone/hexane, 1:1, followed by acetone/dichloromethane, 1:50). The purple fraction was recovered to give the product.

$[H_2Ru_2(C_6Me_6)_2(p\text{-}Br{-}C_6H_4{-}S)][BF_4]$ ([1a][BF_4]): Yield: 40%, 26 mg, 32 μmol. Crystals were obtained by diffusion of diethyl ether in a saturated solution of dichloromethane. ^{1}H NMR (200 MHz, [D_6]acetone, 21 °C): δ = −16.69 (d, ^2J = 3 Hz, 1 H, hydride), −13.07 (d, ^2J = 3 Hz, 1 H, hydride), 2.28 (s, 36 H, $C_6(CH_3)_6$], 7.19 (d, ^3J = 8 Hz, 2 H, *H*-Ar), 7.50 (d, ^3J = 8 Hz, 2 H, *H*-Ar) ppm. ^{13}C{^{1}H} NMR (50 MHz, [D6]acetone, 21 °C): δ = 17.3 (Ru−C−CH_3), 95.6 (Ru−*C*−CH_3), 120.8 (*C*−Br), 131.2 (*C*−H Ar), 135.5 (*C*−H Ar), 141.1 (*C*−S) ppm. MS (ESI): *m*/*z* = 717 [M^+ + H]. $C_{30}H_{42}BBrF_4Ru_2S$ (803.57): calcd. C 43.14, H 5.43; found C 43.60, H 5.71.

$[H_2Ru_2(C_6Me_6)_2(p\text{-}Me{-}C_6H_4{-}S)][BF_4]$ ([1b][BF_4]): Yield: 43%, 26 mg, 35 μmol. ^{1}H NMR (200 MHz, [D_6]acetone, 21 °C): δ = −16.75 (d, ^2J = 3.4 Hz, 1H, hydride), −12.88 (d, ^2J = 3.4 Hz, 1H. hydride), 2.26 [s, 36 H, $C_6(CH_3)_6$], 7.09 (d, ^3J = 8.6 Hz, 2 H, *H*-Ar), 7.15 (d, ^3J = 8.6 Hz, 2 H, *H*-Ar) ppm. ^{13}C{^{1}H} NMR (50 MHz, [D_6]acetone, 21 °C): δ = 17.2 (Ru−C−CH_3), 20.4 (S−C_6H_4−CH_3), 95.4 (Ru−*C*−CH_3), 129.0 (*C*-Ar), 133.5 (*C*-Ar), 137.1 (*C*-Ar), 137.6 (*C*−S) ppm. MS (ESI): *m*/*z* = 652 [M^+ + H]. $C_{31}H_{45}BF_4Ru_2S$ (738.7): calcd. C 50.40, H 6.14; found C 50.62, H 6.25.

Preparation of $[H_2Ru_2(1,2,4,5\text{-}Me_4C_6H_2)_2(p\text{-}X{-}C_6H_4{-}S)][BF_4]$: The dinuclear trihydrido salt $[H_3Ru_2(1,2,4,5\text{-}Me_4C_6H_2)_2][BF_4]$ (40 mg, 71 μmol) and *p*-bromothiophenol (14.55 mg, 77 μmol) or *p*-thiocresol (9.56 mg, 77 μmol) were dissolved in degassed technical grade dichloromethane (60 mL) and heated at 50 °C for 16 hours. After cooling to room temperature, the red solution was filtered, and the solvent was evaporated to dryness under reduced pressure. The red solid was washed with diethyl ether (3 × 20 mL), dissolved in dichloromethane, and isolated by preparative thin-layer chromatography on silica (eluent: acetone/hexane 1:1, followed by acetone/dichloromethane, 1:50). The purple fraction was recovered to give the product.

$[H_2Ru_2(1,2,4,5\text{-}Me_4C_6H_2)_2(p\text{-}Br{-}C_6H_4{-}S)][BF_4]$ ([1c][BF_4]): Yield: 6%, 3.2 mg, 4 μmol. ^{1}H NMR (200 MHz, [D_6]acetone, 21 °C): δ = −16.20 (d, ^2J = 2.9 Hz, 1 H, hydride), −12.38 (d, ^2J = 2.9 Hz, 1 H, hydride), 2.13 (s, 12H, ($C_6H_2(CH_3)_4$], 2.35 (s, 12H, ($C_6H_2(CH_3)_4$], 5.93 (s, 4H, *H*-Ar), 7.33 (d, ^3J = 8.5 Hz, 2H, *H*-Ar), 7.45 (d, ^3J = 8.5 Hz, 2H, *H*-Ar) ppm. MS (ESI): *m*/*z* = 661 [M^+ + H]. $C_{26}H_{34}BBrF_4Ru_2S$ (747.46): calcd. C 41.78, H 4.58; found C 41.62, H 4.67.

$[H_2Ru_2(1,2,4,5\text{-}Me_4C_6H_2)_2(p\text{-}Me{-}C_6H_4{-}S)][BF_4]$ ([1d][BF_4]): Yield: 6%, 3 mg, 4 μmol. ^{1}H NMR (200 MHz, [D_6]acetone, 21 °C): δ = −16.35 (d, ^2J = 3.4 Hz, 1 H, hydride), −12.25 (d, ^2J = 3.4 Hz, 1 H, hydride), 2.08 (s, 12H, $C_6H_4(CH_3)_4$], 2.31 (s, 3 H, Ar-CH_3), 2.33 (s, 12H, $C_6H_2(CH_3)_4$], 5.87 (s, 4 H, *H*-Ar), 7.10 (d, ^3J = 7.8 Hz, 2 H, *H*-Ar), 7.21 (d, ^3J = 7.8 Hz, 2 H, *H*-Ar) ppm. MS (ESI): *m*/*z* = 596 [M^+ + H]. $C_{27}H_{37}BF_4Ru_2S$ (682.6): calcd. C 47.51, H 5.46; found C 47.37, H 5.39.

Preparation of $[HRu_2(C_6Me_6)_2(p\text{-}X{-}C_6H_4{-}S)_2][BF_4]$: The dinuclear trihydrido salt $[H_3Ru_2(C_6Me_6)_2][BF_4]$ (60 mg, 97 μmol) and *p*-bromothiophenol (37 mg, 196 μmol) or *p*-thiocresol (24 mg, 196 μmol) were dissolved in degassed technical grade ethanol (60 mL) and heated under reflux for 16 hours. After cooling to room temperature, the red solution was filtered, and the solvent was evaporated to dryness under reduced pressure. The red solid obtained

was washed with diethyl ether (3 × 20 mL), dissolved in dichloromethane, and isolated by preparative thin-layer chromatography on silica (eluent: acetone/hexane 1:1, followed by acetone/dichloromethane 1:50). The red fraction was recovered to give the product.

[$HRu_2(C_6Me_6)_2$(*p*-Br−C_6H_4−S)$_2$][BF_4] ([2a][BF_4]): Yield: 67%, 64 mg, 65 μmol. Crystals were obtained by diffusion of diethyl ether in a saturated solution of dichloromethane. ^{1}H NMR (200 MHz, [D$_6$]acetone, 21 °C): δ = −11.97 (s, 1H, hydride), 2.22 (s, 36H, $C_6(CH_3)_6$], 7.6−7.1 (m, 4 H, *H*-Ar); ^{13}C{^{1}H} NMR (50 MHz, [D$_6$]acetone, 21 °C): δ = 16.7 (Ru−C−CH_3), 98.1 (Ru−*C*−CH_3), 121.5 (*C*−Br), 131.5 (*C*-Ar), 135.2 (*C*-Ar), 137.7 (*C*−S) ppm. MS (ESI): *m*/*z* = 903 [M$^+$ + H]. $C_{36}H_{45}BBr_2F_4Ru_2S_2$ (990.6): calcd. C 45.11, H 4.73; found C 45.52, H 4.81.

[$HRu_2(C_6Me_6)_2$(*p*-Me−C_6H_4−S)$_2$][BF_4] ([2b][BF_4]): Yield: 65%, 54 mg, 63 μmol. ^{1}H NMR (200 MHz, [D$_6$]acetone, 21 °C): δ = −11.97 (s, 1 H, hydride), 2.17 (s, 36 H, $C_6(CH_3)_6$], 2.31 (s, 6 H, Ar-CH_3), 7.4−7.0 (m, 4 H, *H*-Ar); ^{13}C{^{1}H} NMR (50 MHz, [D$_6$]acetone, 21 °C): δ = 16.5 (Ar-*C*H$_3$), 16.8 (Ru−C−*C*H$_3$), 97.7 (Ru−*C*−H), 129.3 (*C*-Ar), 133.5 (*C*-Ar), 137.4 (*C*−S) ppm. MS (ESI): *m*/*z* = 774 [M$^+$ + H]. $C_{38}H_{51}BF_4Ru_2S_2$ (860.89): calcd. C 53.02, H 5.97; found C 52.88, H 6.11.

Preparation of [HRu_2(1,2,4,5-$Me_4C_6H_2$)$_2$(*p*-X−C_6H_4−S)$_2$][BF_4]: The dinuclear trihydrido salt [H_3Ru_2(1,2,4,5-$Me_4C_6H_2$)$_2$][BF_4] (40 mg, 71 μmol) and *p*-bromothiophenol (30 mg, 160 μmol) or *p*-thiocresol (20 mg, 160 μmol) were dissolved in dichloromethane (40 mL) and heated under reflux for 16 hours. After cooling to room temperature, the red solution was filtered, and the solvent was evaporated to dryness under reduced pressure. The red solid was washed with diethyl ether (3 × 20 mL), dissolved in dichloromethane, and isolated by preparative thin-layer chromatography on silica (eluent: acetone/hexane, 1:1, followed by acetone/dichloromethane, 1:50). The red fraction was recovered to give the product.

[HRu_2(1,2,4,5-$Me_4C_6H_2$)$_2$(*p*-Br−C_6H_4−S)$_2$][BF_4] ([2c][BF_4]): Yield: 67%, 45 mg, 48 μmol. Crystals were obtained by diffusion of diethyl ether into a saturated solution of dichloromethane. ^{1}H NMR (200 MHz, [D$_6$]DMSO, 21 °C): δ = −11.24 (s, 1H, hydride), 1.72 (s, 12 H, $C_6H_2(CH_3)_4$], 2.25 (s, 12 H, $C_6H_2(CH_3)_4$], 6.01 (s, 4 H, $C_6H_2(CH_3)_4$], 7.6−7.2 (m, 8 H, *H*-Ar) ppm. ^{13}C{^{1}H} NMR (50 MHz, [D$_6$]DMSO, 21 °C): δ = 17.4 (Ru−C−*C*H$_3$), 18.8 (Ru−C−*C*H$_3$), 89.7 (Ru−*C*−CH$_3$), 99.3 (Ru−*C*−CH$_3$), 100.9 (Ru−*C*−H), 131.5 (*C*−Br), 131.9 (*C*−Br), 134.3 (*C*-Ar), 134.9 (*C*-Ar), 135.9 (*C*-Ar), 136.5 (*C*−S), 139.8 (*C*−S) ppm. MS (ESI): *m*/*z* = 848 [M$^+$ + H]. $C_{32}H_{37}BBr_2F_4Ru_2S_2$ (934.52): calcd. C 41.12, H 3.99; found C 41.84, H 4.19.

[HRu_2(1,2,4,5-$Me_4C_6H_2$)$_2$(*p*-Me−C_6H_4−S)$_2$][BF_4] ([2d][BF_4]): Yield: 70%, 40 mg, 50 μmol. Crystals were obtained by diffusion of diethyl ether into a saturated solution of dichloromethane. ^{1}H NMR (200 MHz, [D$_6$]acetone, 21 °C): δ = −11.12 (s, 1 H, hydride), 1.85 (s, 12 H, $C_6H_2(CH_3)_4$], 2.28 (s, 3 H, Ar-C*H*$_3$), 2.33 (s, 3 H, Ar-C*H*$_3$), 2.38 (s, 12 H, $C_6H_2(CH_3)_4$], 5.95 (s, 4 H, $C_6H_2(CH_3)_4$], 7.10 (d, ^3J = 8.2 Hz, 2 H, *H*-Ar), 7.11 (d, ^3J = 8.2 Hz, 2 H, *H*-Ar), 7.29 (d, ^3J = 8.2 Hz, 2H, *H*-Ar), 7.46 (d, ^3J = 8.2 Hz, 2 H, *H*-Ar) ppm. ^{13}C{^{1}H} NMR (50 MHz, [D$_6$]DMSO, 21 °C): δ = 16.6 (Ru−C−*C*H$_3$), 17.9 (Ru−C−*C*H$_3$), 20.5 (Ar-*C*H$_3$), 20.6 (Ar-*C*H$_3$), 89.6 (Ru−*C*−CH$_3$), 91.7 (Ru−*C*−H), 98.5 (Ru−*C*−H), 99.2 (Ru−*C*−H), 100.3 (Ru−*C*−H), 129.0 (*C*-Ar), 129.3 (*C*-Ar), 129.6 (*C*-Ar), 130.6 (*C*-Ar), 132.9 (*C*-Ar), 133.3 (*C*-Ar), 134.1 (*C*-Ar), 136.9 (*C*−S), 138.2 (*C*−S) ppm. MS (ESI): *m*/*z* = 848 [M$^+$ + H]. $C_{32}H_{37}BBr_2F_4Ru_2S_2$ (934.52): calcd. C 41.12, H 3.99; found C 41.84, H 4.19.

Preparation of [$HRu_2(C_6Me_6)_2$(*p*-C_4H_3S−C_6H_4−S)$_2$][BF_4] ([3][BF_4]): The dinuclear hydrido salt [$HRu_2(C_6Me_6)_2$(*p*-S−C_6H_4−Br)$_2$][BF_4] (50 mg, 56 μmol) and 3-thiophene boronic acid (20.5 mg, 160 μmol) were dissolved in distilled ethanol

Table 2. Crystallographic and selected experimental data of [**1a**][BF_4], [**2a**][BF_4], [**2c**][BF_4], [**2d**][BF_4], and [**3**][BF_4]

	[**1a**][BF_4]·C_6H_6	[**2a**][BF_4]·$CO(CH_3)_2$	[**2c**][BF_4]	[**2d**][BF_4]	[**3**][BF_4]·CH_2Cl_2
Chemical formula	$C_{36}H_{48}BBrF_4Ru_2S$	$C_{39}H_{51}BBr_2F_4ORu_2S_2$	$C_{32}H_{37}BBr_2F_4Ru_2S_2$	$C_{34}H_{43}BF_4Ru_2S_2$	$C_{45}H_{53}BCl_2F_4Ru_2S_4$
Molecular mass	881.66	1048.69	934.51	804.75	1081.96
Crystal system	monoclinic	triclinic	monoclinic	triclinic	triclinc
Space group	*Cc*	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
Color and shape	red plate	red rod	red block	red block	orange plate
Crystal size	0.40 × 0.08 × 0.04	0.28 × 0.08 × 0.08	0.25 × 0.25 × 0.15	0.32 × 0.26 × 0.24	0.48 × 0.25 × 0.05
a (Å)	16.144(1)	11.906(1)	11.3006(6)	11.775(2)	10.731(1)
b (Å)	15.021(1)	13.600(1)	16.872(1)	11.796(1)	14.166(2)
c (Å)	15.856(1)	14.603(1)	18.383(1)	12.374(2)	16.975(3)
α (°)	90	72.62(1)	90	93.00(2)	87.39(2)
β (°)	111.400(9)	81.35(1)	90.700(7)	94.01(1)	73.87(1)
γ (°)	90	84.41(1)	90	101.19(2)	70.03(1)
V (Å^3)	3580.1(6)	2227.3(4)	3504.5(4)	1678.1(4)	2326.1(6)
Z	4	2	4	2	2
T (K)	153(2)	153(2)	293(2)	153(2)	153(2)
D_c (g·cm^{-3})	1.636	1.564	1.771	1.593	1.545
μ (mm^{-1})	2.063	2.610	3.304	1.070	0.991
Scan range (°)	3.84 < 2θ < 52.88	4.26 < 2θ < 51.92	4.20 < 2θ < 51.90	4.48 < 2θ < 52.16	4.06 < 2θ < 51.90
Unique reflections	6537	8111	6816	6163	8373
Reflections used [$I > 2\sigma(I)$]	3505	5997	4443	4834	2936
R_{int}	0.0832	0.0294	0.0528	0.0337	0.1198
Final *R* indices[$I > 2\sigma(I)$]	0.1203, wR_2 0.3025	0.0327, wR_2 0.0769	0.0339, wR_2 0.0723	0.0264, wR_2 0.0626	0.0704, wR_2 0.1496
R indices (all data)	0.1878, wR_2 0.3499	0.0501, wR_2 0.0846	0.0633, wR_2 0.0779	0.0376, wR_2 0.0666	0.1725, wR_2 0.1726
Goodness-of-fit	1.089	0.918	0.857	0.939	0.735
Max, Min Δρ/e (Å^{-3})	4.264, -2.093	1.079, −0.870	1.007, −0.606	0.495, −1.082	0.773, −0.651

(15 mL). Sodium carbonate (17 mg, 160 μmol) and tetrakis(triphenylphosphane)palladium (12 mg, 16 μmol) were then added to the solution, which was heated under reflux for four days. After cooling to room temperature, the red-brown solution was filtered, and the solvent was evaporated to dryness under reduced pressure. The red solid was dissolved in dichloromethane and purified by preparative thin-layer chromatography on silica (eluent: acetone/hexane, 1:1, acetone/dichloromethane, 1:50). The red fraction containing the desired product was collected. Yield: 14%, 8 mg, 8 μmol. Crystals were obtained by diffusion of diethyl ether into a saturated solution of dichloromethane. The MS (ESI) spectra shows the molecular peak [M^+ + H] m/z = 910 and two other peaks corresponding to the loss of one and two thienyl groups (m/z = 827, m/z = 744). ^{1}H NMR (200 MHz, [D6]acetone, 21 °C): δ = −11.89 (s, 1 H, hydride), 2.23 [s, 36 H, $C_6(CH_3)_6$], 7.93−7.24 (m, 14 H, S−C_6H_4−C_4H_3S) ppm. for $C_{44}H_{51}BF_4Ru_2S_4$ (997.1): calcd. C 53.00, H 5.16; found C 49.87, H 5.19.

X-ray Crystallographic Study: The data were measured on a Stoe Image Plate Diffraction system equipped with a φ circle, using Mo-K_α graphite-monochromated radiation (λ = 0.71073 Å) with φ range 0−200°, increment ranging from 1.0−1.8°, 2θ range from 2.0−26°, $D_{max}-D_{min}$ = 12.45−0.81 Å. The structures were solved by direct methods with the program SHELXS-97.[19] The refinement and all further calculations were carried out using SHELXL-97.[20] The H-atoms were included in calculated positions and treated as riding atoms with the SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-square on F^2. Figures were drawn with ORTEP.[21] All crystallographic data are collected in Table 2. CCDC-220959 for [**1a**][BF_4], -220962 for [**2a**][BF_4], -220961 for [**2c**][BF_4], -220960 for [**2d**][BF_4], and -220963 for [**3**][BF_4] contain the supplementary crystallographic data. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk]

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