Synthesis, molecular structure and electrochemical properties of the star-shaped dinuclear complexes [Ru$_2$(η^6-p-Me–C$_6$H$_4$-^{i}Pr)$_2$(μ$_2$-S-p-C$_6$H$_4$–C$_4$H$_3$S)$_3$]$^+$ and [Rh$_2$(η^5-C$_5$Me$_5$)$_2$(μ$_2$-S-p-C$_6$H$_4$–C$_4$H$_3$S)$_3$]$^+$
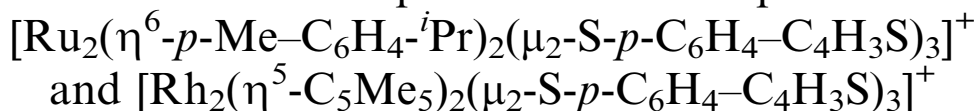
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Abstract

The dinuclear cations [Ru$_2$(η^6-p-Me–C$_6$H$_4$–^{i}Pr)$_2$(μ$_2$-S-p-C$_6$H$_4$–Br)$_3$]$^+$ and [Rh(η^5-C$_5$Me$_5$)(μ$_2$-S-p-C$_6$H$_4$–Br)$_3$]$^+$ are found to undergo triple Suzuki coupling with 2- or 3-thiophene boronic acid to give [Ru$_2$(η^6-p-Me–C$_6$H$_4$–^{i}Pr)$_2$(μ$_2$-S-p-C$_6$H$_4$–C$_4$H$_3$S)$_3$]$^+$ (**1** and **2**) and [Rh$_2$(η^5-C$_5$Me$_5$)$_2$(μ$_2$-S-p-C$_6$H$_4$–C$_4$H$_3$S)$_3$]$^+$ (**3** and **4**), respectively. The star-like complexes are potential precursors for the insertion of dinuclear organometallic entities in the main chain of conjugated molecules thanks to their free thienyl moieties at their periphery. The electrochemical and optical properties of these new complexes have also been investigated.
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1. Introduction

Star-shaped molecules have been extensively investigated since 1980, because this arrangement can lead to a strong enhancement of the physical properties in hyperbranched conjugated polymers such as nonlinear optical susceptibilities [1–3], electronic conductivities [4] or light-emitting applications [5,6]. Moreover, there is an increasing interest for conjugated oligomers because of their intrinsic physical properties [7,8] as well as in model compounds for the study of corresponding conductive polymers [9]. Oligothiophenes or polythiophenes are used, because their electronic properties can be tuned by chemical modifications to allow many technological applications based on reversible reduction–oxidation properties [10–12]. On the other hand, conjugated polymers containing metal centers have been investigated because of their electronic, nonlinear optical, magnetic, catalytic properties [13–15] and in the development of sensors [16,17]. Despite the large number of new compounds synthesized in these fields of research, little is known about star-shaped molecules containing a dinuclear metal core. To the best of our knowledge, more than 99% of star-shaped molecules are built around mononuclear building blocks that are coordinated to ligands such as salens, dithiolenes or

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"nitrogen bridges" (terpyridines, bipyridines or porphyrins) [13,18]. However, there are still challenges to develop versatile and selective strategies in the view of creating new molecular design and new bridging ligands. For example, Shin et al. [19] have very recently described octahedral dinuclear complexes, based on two molybdenum centers and four sulfur atoms, which are functionalized by two alkynylterthienyl moieties. On the other hand, we have described the first examples of dinuclear organometallic species (ruthenium or rhodium derivatives) in star-like conjugated molecules with sulfur connectivities of the type $[Ru_2(\eta^6\text{-}p\text{-Me–}C_6H_4\text{–}^iPr)_2(\mu_2\text{-S-}p\text{-}C_6H_4\text{–X})_3]^+$ and $[Rh_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-S-}p\text{-}C_6H_4\text{–X})_3]^+$, where X is a functional group such as OH [20,21] or Br [22,23]. In addition, we have developed a method to obtain new π-conjugated materials, based on dinuclear (arene)ruthenium complexes, functionalized with one or two sulfur connectivities [24]. In this paper, we present new complexes obtained by Suzuki cross coupling reactions between $[Ru_2(\eta^6\text{-}p\text{-Me–}C_6H_4\text{–}^iPr)_2(\mu_2\text{-S-}p\text{-}C_6H_4\text{–Br})_3]^+$ and $[Rh_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-S-}p\text{-}C_6H_4\text{–}$ Br$)_3]^+$ and thiophene boronic acids as well as their electrochemical and optical properties.

2. Results and discussion

The cationic complexes $[Ru_2(\eta^6\text{-}p\text{-Me–}C_6H_4\text{–}^iPr)_2(\mu_2\text{-}$ S-p-C_6H_4–Br$)_3]^+$ and $[Rh_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-S-}p\text{-}C_6H_4\text{–}$ Br$)_3]^+$ react in ethanol with 2-thiophene or 3-thiophene boronic acids: In the presence of Pd(PPh$_3$)$_4$ as catalyst, to give the conjugated complexes 1–4, respectively, isolated as the chloride salts with yields ranging from 75% to 85% (See Scheme 1). Only the formation of trisubstituted compounds is observed.

All cations 1–4 were characterized by MS and spectroscopic data (IR, ^{1}H and ^{13}C NMR) as well as by satisfactory elemental analysis data of the chloride salts. The chloride salts are only soluble in alcohols, while the bromide salts, accessible by anion exchange, are slightly soluble in chlorinated solvents and acetone but insoluble in water. The molecular structures of 3 and
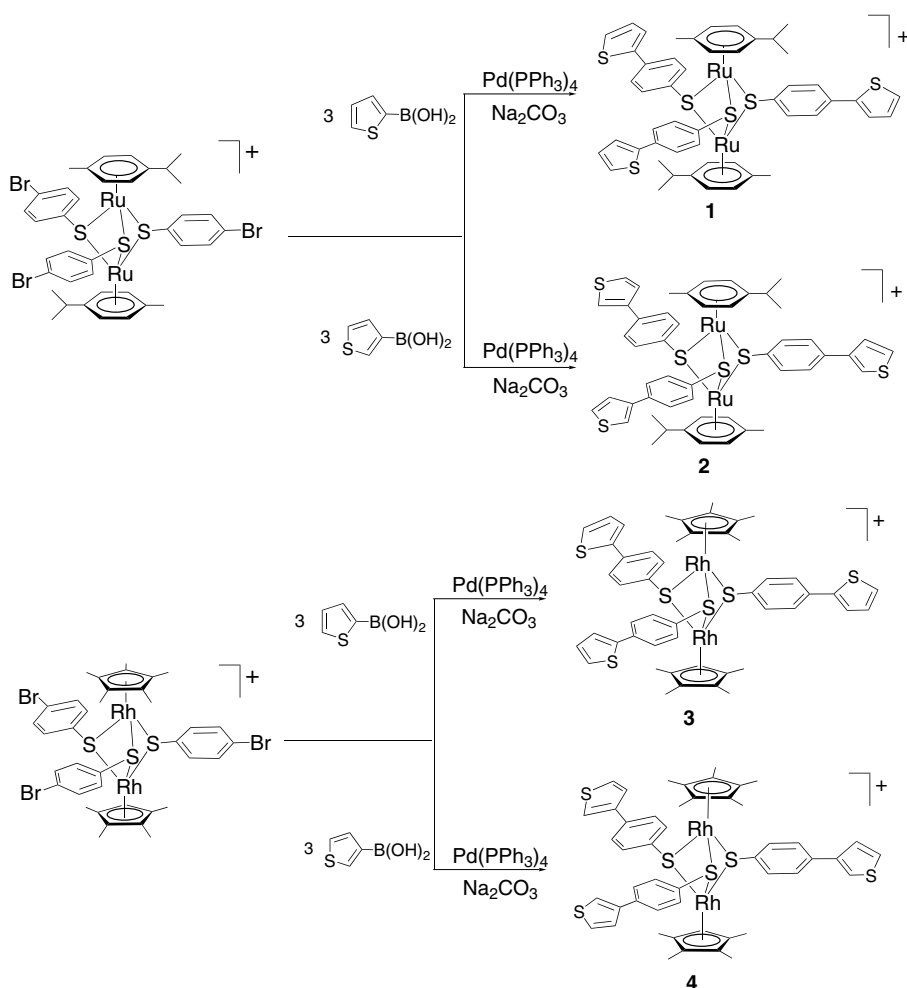
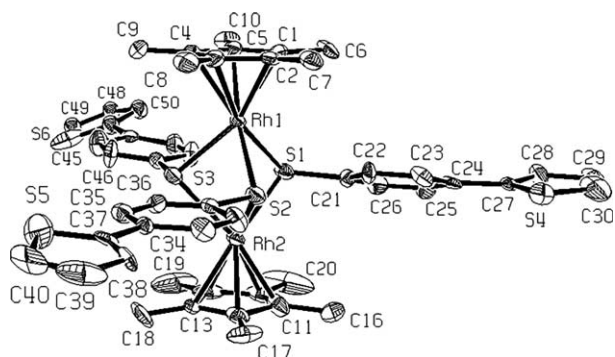Scheme 1. Synthesis of star-shaped conjugated cations 1–4.

Fig. 1. Molecular structure of **3**, hydrogen atoms, anion and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Rh(1)–S(1) 2.401(3), Rh(1)–S(2) 2.400(3), Rh(1)–S(3) 2.400(3), Rh(2)–S(1) 2.402(3), Rh(2)–S(2) 2.395(3), Rh(2)–S(3) 2.388(3), Rh(1)–Rh(2) 3.2168(11), Rh(1)–S(1)–Rh(2) 84.10(10), Rh(1)–S(2)–Rh(2) 84.26(11), Rh(1)–S(3)–Rh(2) 84.42(10).

4, shown in Figs. 1 and 2, were confirmed by a single-crystal X-ray structure analysis of their bromide salts.

The cations **3** and **4** are found to consist of a closed trigonal bipyramid Rh_2S_3 framework, each rhodium atom being coordinated to an η^5-C_5Me_5 ligand, and each sulfur atom carrying a p-(2′-thienyl)phenyl or p-(3′-thienyl)phenyl group respectively. The Rh–S bond distances [ranging from 2.381 to 2.420 Å] and Rh–S–Rh angles [ranging from 84.10° to 85.20°] are similar to those found in other dinuclear η^5-C_5Me_5 rhodium complexes triply bridged by sulfur atoms; $[Rh_2(C_5Me_5)_2(SH)_3]^+$ [25], $[Rh_2(C_5Me_5)_2(S–C_6F_5)_3]^+$ [26], $[Rh_2(C_5Me_5)_2(S–CH_3)_3]^+$ [27], $[Rh_2(C_5Me_5)_2(S–C_6H_5)_3]^+$ [28], $[Rh_2(C_5Me_5)_2(S–^iPr)_3]^+$ [28], $[Rh_2(C_5-$
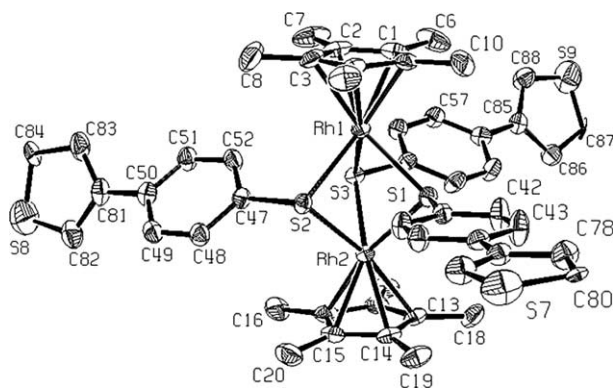

Fig. 2. Molecular structure of molecule A of **4**, the second independent molecule B, hydrogen atoms, anion and chloroform molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Rh(1)–S(1) 2.3811(10), Rh(1)–S(2) 2.3955(10), Rh(1)–S(3) 2.4052(10), Rh(2)–S(1) 2.3918(10), Rh(2)–S(2) 2.4174(10), Rh(2)–S(3) 2.3792(10), Rh(1)–Rh(2) 3.2306(4), Rh(3)–S(4) 2.3807(10), Rh(3)–S(5) 2.4196(10), Rh(3)–S(6) 2.3899(10), Rh(4)–S(4) 2.3897(10), Rh(4)–S(5) 2.3905(10), Rh(4)–S(6) 2.3939(10), Rh(3)–Rh(4) 3.2237(4), Rh(1)–S(1)–Rh(2) 85.20(3), Rh(1)–S(2)–Rh(2) 84.32(3), Rh(1)–S(3)–Rh(2) 84.94(3), Rh(3)–S(4)–Rh(4) 85.03(3), Rh(3)–S(5)–Rh(4) 84.16(3), Rh(3)–S(6)–Rh(4) 84.74(3).

$Me_5)_2(\mu_2$-S-p-C_6H_4–OH)$_3]^+$ [20], $[Rh_2(C_5Me_5)_2(\mu_2$-S-p-C_6H_4–Br)$_3]^+$ [22], and $[Rh_2(C_5Me_5)_2(\mu_2$-S-p-C_6H_4–Ph)$_3]^+$ [22]. Because of the relatively large separation between the two rhodium centers as well as the limited number of substituents attached to the arene ligands, in the cations **3** and **4** the three phenyl rings of the p-phenyl-thiolato derivative ligands are not constrained to a coplanar arrangement. In **3**, where the thienyl units are almost coplanar with the phenyls, the three phenyl rings are only rotated by 1.7°, 4.3° and 20.3°, respectively, with respect to the plane formed by the three coordinated sulfur atoms. However in **4**, where two almost identical independent molecules are found per asymmetric unit, the three phenyl rings which are rotated by 2.1°, 29.9° and 37.7° in molecule A, 11.7°, 14.6° and 24.0° in molecule B, show non-coplanar thienyl units.

The UV–Vis spectra of the ruthenium complexes **1** and **2** show, due to the aromatic ligands, only π–π* transition bands (315 nm), see Fig. 3. The same π–π* bands are observed around 335 nm for the rhodium complexes **3** and **4**. However, the rhodium complexes show an extra band centered at 420 nm ($\varepsilon \cong 18,000$ mol^{-1} cm^{-1} l) which can be attributed to metal ligand charge transfer (MLCT). The weaker electron-donor strength of the p-cymene ligands as compared to that of Cp*, which leads to a blue-shift of their MLCT band, explains the absence of a MLCT band in the UV–Vis spectra of the ruthenium complexes.

The electrochemical behavior of complexes **1**–**4** have been investigated in oxidation as well as in reduction. In the case of the oxidation process, a first experiment has been performed up to 1.2 V and the corresponding cyclic voltamograms have been recorded (see Fig. 4).

All complexes exhibit a first oxidation state, E_{pA1}, which can be assigned to the irreversible oxidation of μ_2-sulfur bridge (see Table 1). The peak corresponding to the reduction of this bridge is only observed in complex **4** (E_{pC1} at −0.090 V).

The ruthenium complexes show a second reversible oxidation state, E_{pA2}, close to 1.03 V, which is assigned to the redox couple RuIII/RuII with a ΔE_p of 0.264 and 0.206 V for complexes **1** and **2**, respectively. These potentials are close to those observed in chloro arene–ruthenium complexes [29,30] but higher than those found for complexes of the type bis(2,2′-bipyiridine)-dithiolato-ruthenium [31] (close to 0.05V). The radical cations formed during the oxidation of **2** are electrochemically stable. In the case of the rhodium complexes, the second oxidation state E_{pA2}, assigned to RhIV/RhIII, is irreversible. Therefore, the generated radical cations are unstable.

Additional measurements for the oxidation of complexes **1**–**4** have been performed at higher potentials than those presented in Fig. 4. In the case of complexes with only one free α position in the thienyl moieties, i.e., complexes **1** and **3**, only one irreversible peak is
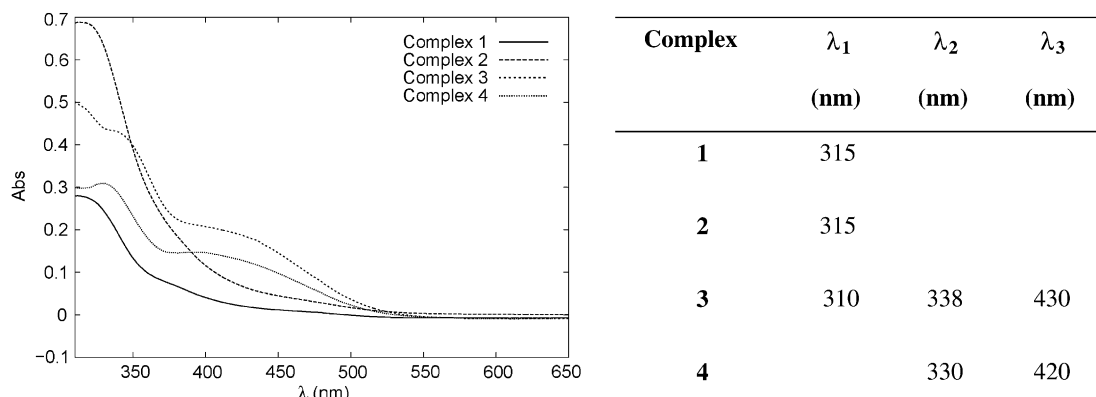
Complex	λ_1	λ_2	λ_3
	(nm)	(nm)	(nm)
1	315		
2	315		
3	310	338	430
4		330	420

Fig. 3. Absorption spectra of **1–4** in dichloromethane (conc. 1.1×10^{-5} mol l^{-1}) and a list of the corresponding absorption wavelength.
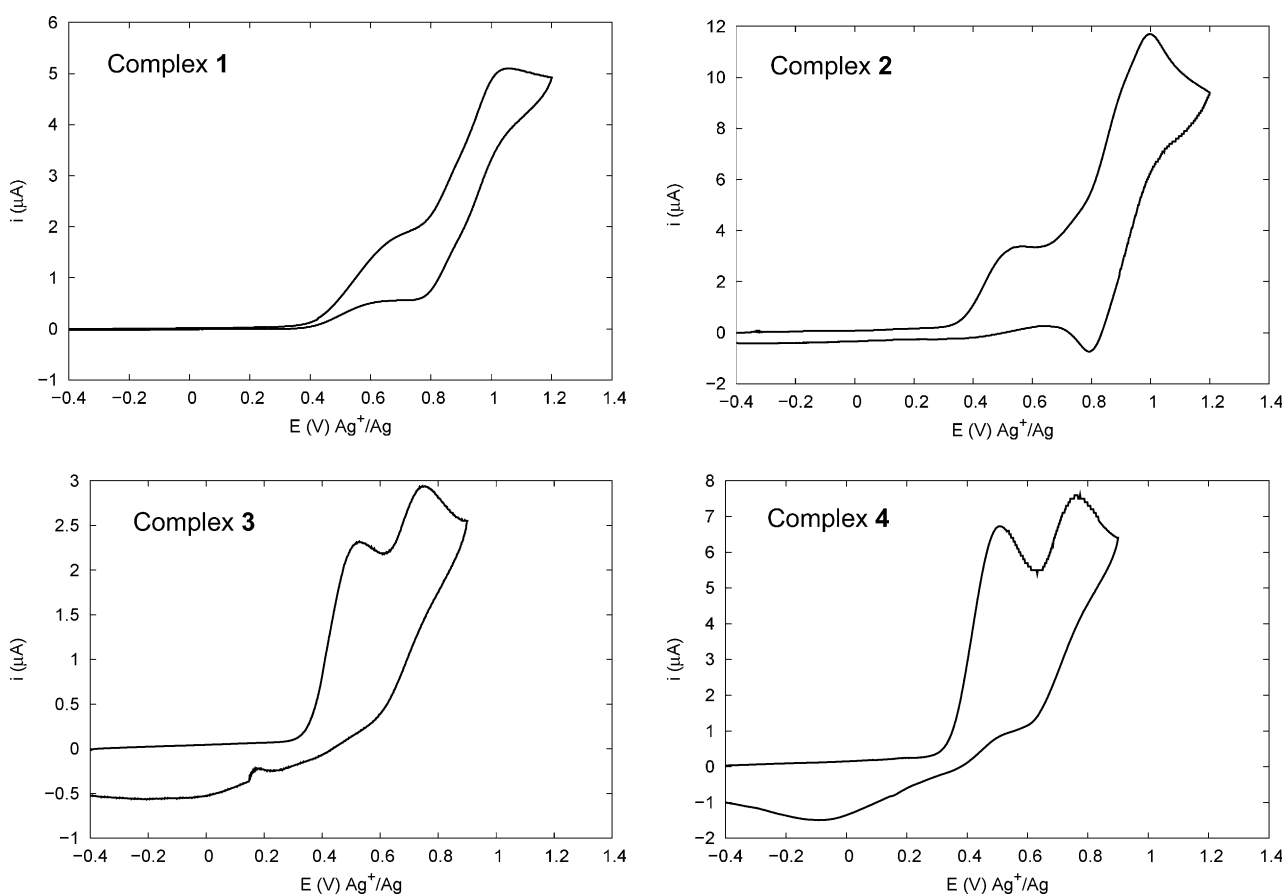

Fig. 4. Cyclic voltamograms (range −0.4 to 1.2 V) of complexes **1–4** (conc. 1.1×10^{-3} mol l^{-1}) in dichloromethane. Supporting electrolyte 0.1 mol l^{-1} NBu$_4$PF$_6$, on a platinum disc working electrode (reference 10^{-2} M Ag$^+$/Ag); scan rate: 100 mV s^{-1}.

observed at 1.242 and 1.403 V, respectively. It can be attributed to the formation of a radical cation at the α position [11]. Accordingly complex **2** which possesses two free α positions at each thienyl moieties, exhibits two irreversible peaks at 1.450 and 1.224 V. They can be attributed to the formation of two radical cations at these free positions [11]. However, only one reversible peak is observed at 1.404 V for complex **4** indicating that only one radical cation is formed. In addition, several

other experiments have been performed to check the electrochemical behavior of these complexes. Redox forms of complexes **1–4** are electrochemically stable during electrochemical cyclability (10 cycles, $v = 100$ mV s^{-1}). A series of cyclic voltammograms are also realized as a function of scan rate between 20 and 100 mV s^{-1}. The evolution of the anodic and cathodic peak current is linear as a function of the square scan rate, which indicates a diffusion limiting process.

Table 1
Cyclic voltammetry data for oxidation of complexes **1**–**4** (conc. 1.1×10^{-3} mol l^{-1}) in dichloromethane

Complex	E_{pA1} (V)	E_{pA2} (V)	E_{pC1} (V)	E_{pC2} (V)
1	0.722	1.060		0.746
2	0.552	0.998		0.792
3	0.524	0.756		0.595
4	0.510	0.764	−0.090	0.566

Supporting electrolyte 0.1 mol l^{-1} NBu$_4$PF$_6$, on a platinum disc working electrode (reference 10^{-2} M Ag$^+$/Ag); scan rate: 100 mV s^{-1}.

The reduction of the complexes has been also investigated. All complexes exhibit one irreversible peak at −1.450 V for ruthenium and −1.350 V for the rhodium derivatives. This can be assigned to the reduction of the aromatic ligands, *p*-cymene and Cp*, respectively [32]. The difference of potential is related to the red-shift of MLCT band in the UV–Vis spectra, because the energy required to reduce the aromatic ligand is lower in the case of Cp* than in that of *p*-cymene. However, no electropolymerization of complexes has been observed. This is due to the incompatibility of the oxidation potential of the metal center and the thienyl moiety. One solution to unravel this problem is to increase the number of thienyl units on each arm to decrease their oxidation potential.

3. Experimental

3.1. General remarks

All reactions were carried out under nitrogen using standard Schlenk techniques. Solvents were degassed prior to use. The dinuclear dichloro complexes [Ru(*p*-Me–C$_6$H$_4$–^{i}Pr)Cl$_2$]$_2$ [33,34] and [Rh(C$_5$Me$_5$)Cl$_2$]$_2$ [35] as well as the salts [Ru$_2$(*p*-Me–C$_6$H$_4$–^{i}Pr)$_2$(μ_2-S-*p*-C$_6$H$_4$–Br)$_3$]Cl [22] and [Rh$_2$(C$_5$Me$_5$)$_2$(μ_2-S-*p*-C$_6$H$_4$–Br)$_3$]Cl [22] were synthesized according to literature methods.

All other reagents were purchased (Aldrich or Acros) and used as received. NMR spectra were recorded with 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).

3.2. Syntheses

3.2.1. General method for 1–4

The salt [Ru$_2$(*p*-Me–C$_6$H$_4$–^{i}Pr)$_2$(μ_2-S-*p*-C$_6$H$_4$–Br)$_3$]Cl (107 mg, 0.1 mmol) or [Rh$_2$(C$_5$Me$_5$)$_2$(μ_2-S-*p*-C$_6$H$_4$–Br)$_3$]Cl (108 mg, 0.1 mmol) and 2- or 3-thiophene boronic acid (45 mg, 0.35 mmol) were dissolved in technical grade ethanol. Then, an aqueous solution of Na$_2$CO$_3$

(1 ml, 2 N) and Pd(PPh$_3$)$_4$ (0.01 mmol, 11 mg) was added. The resulting mixture was refluxed in ethanol for 48 h. After cooling to 20 °C, the red solution was filtered through Celite, and the solvent was removed under reduced pressure. The oil obtained was purified by column chromatography (silica gel, dichloromethane/ethanol 10:1, r_f close to 0.8). The cations were isolated in the form of their chloride salts, after evaporation of the solvent, as red-orange powders. The corresponding bromo salts were prepared by anion exchange by adding an equimolar amount of KBr to the suspension of **1**–**4** in chloroform and, after filtration through Celite, by removing the solvent under reduced pressure.

3.2.2. [Ru$_2$(η^6-p-Me–C$_6$H$_4$–^{i}Pr)$_2$(μ_2-S-p-C$_6$H$_4$-2'-C$_4$H$_3$S)$_3$]Cl ([1]Cl)

Yield: 92 mg; 85%. ^{1}H NMR (200 MHz, CDCl$_3$, 21 °C): δ = 0.83 (d, $^3J_{H,H}$ = 7.0 Hz, 6H, (CH_3)$_2$CH), 0.93 (d, $^3J_{H,H}$ = 7.0 Hz, 6H, (CH_3)$_2$CH), 1.68 (s, 6H, CH_3), 2.04 (sept, $^3J_{H,H}$ = 7.0 Hz, 2H, (CH$_3$)$_2$CH), 5.21 (d, $^3J_{H,H}$ = 5.9 Hz, 2H, CH–Ar), 5.27 (d, $^3J_{H,H}$ = 5.9 Hz, 2H, CH–Ar), 5.33 (d, $^3J_{H,H}$ = 5.9 Hz, 2H, CH–Ar), 5.56 (d, $^3J_{H,H}$ = 5.9 Hz, 2H, CH–Ar), 7.13 (dd, $^3J_{H,H}$ = 3.6 Hz, $^3J_{H,H}$ = 5.1 Hz, 3H, CH–Ar), 7.34 (dd, $^4J_{H,H}$ = 1.1 Hz, $^3J_{H,H}$ = 5.1 Hz, 3H, CH–Ar), 7.45 (dd, $^4J_{H,H}$ = 1.1 Hz, $^3J_{H,H}$ = 3.6 Hz, 3H, CH–Ar), 7.68 (d, $^3J_{H,H}$ = 8.4 Hz, 6H, CH–Ar), 7.98 (d, $^3J_{H,H}$ = 8.4 Hz, 6H, CH–Ar). ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$, 21 °C): δ = 22.25 (CH$_3$), 22.99 ((CH$_3$)$_2$CH), 27.88 ((CH$_3$)$_2$CH), 30.99 ((CH$_3$)$_2$CH), 84.03 (Ru–C–Ar), 85.31 (Ru–C–Ar), 85.84 (Ru–C–Ar), 100.07 (Ru–C–Ar), 107.85 (Ru–C–Ar), 124.10 (C–Ar), 125.74 (C–Ar), 126.56 (C–Ar), 128.67 (C–Ar), 133.56 (C–Ar), 134.68 (C–Ar), 137.20 (C–Ar), 143.39 (C–Ar), 146.89 (C–S–Ru). MS (ESI) *m/z*: 1045 (M$^+$). Elemental analysis (%) calcd for C$_{50}$H$_{49}$ClRu$_2$S$_6$ (1079.91): C, 55.61; H, 4.57. Found: C, 55.73; H, 4.75%.

3.2.3. [Ru$_2$(η^6-p-Me–C$_6$H$_4$–^{i}Pr)$_2$(μ_2-S-p-C$_6$H$_4$-3'-C$_4$H$_3$S)$_3$]Cl ([2]Cl)

Yield: 80 mg; 75%. ^{1}H NMR (200 MHz, CDCl$_3$, 21 °C): δ = 0.83 (d, $^3J_{H,H}$ = 7.0 Hz, 6H, (CH_3)$_2$CH), 0.93 (d, $^3J_{H,H}$ = 7.0 Hz, 6H, (CH_3)$_2$CH), 1.68 (s, 6H, CH_3), 2.04 (sept, $^3J_{H,H}$ = 7.0 Hz, 2H, (CH$_3$)$_2$CH), 5.21 (d, $^3J_{H,H}$ = 5.9 Hz, 2H, CH–Ar), 5.27 (d, $^3J_{H,H}$ = 5.9 Hz, 2H, CH–Ar), 5.33 (d, $^3J_{H,H}$ = 5.9 Hz, 2H, CH–Ar), 5.55 (d, $^3J_{H,H}$ = 5.9 Hz, 2H, CH–Ar), 7.47 (m, 6H, CH–Ar), 7.51 (dd, $^4J_{H,H}$ = 1.4 Hz, $^3J_{H,H}$ = 2.6 Hz, 3H, CH–Ar), 7.61 (d, $^3J_{H,H}$ = 8.5 Hz, 6H, CH–Ar), 8.05 (d, $^3J_{H,H}$ = 8.5 Hz, 6H, CH–Ar). ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$, 21 °C): δ = 18.06 (CH$_3$), 22.21 ((CH$_3$)$_2$CH), 22.98 ((CH$_3$)$_2$CH), 30.94 ((CH$_3$)$_2$CH), 83.95 (Ru–C–Ar), 85.26 (Ru–C–Ar), 85.84 (Ru–C–Ar), 100.00 (Ru–C–Ar), 107.78 (Ru–C–Ar), 121.25 (C–Ar), 126.32 (C–Ar), 126.97 (C–Ar), 127.20 (C–Ar), 132.25 (C–Ar), 133.51 (C–Ar), 135.92 (C–Ar), 136.85 (C–Ar),

141.27 (C–S-Ru). MS (ESI) m/z: 1045 (M^+). Elemental analysis (%) calcd for $C_{50}H_{49}ClRu_2S_6$ (1079.91): C, 55.61; H, 4.57. Found: C, 55.68; H, 4.78%.

3.2.4. $[Rh_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}S\text{-}p\text{-}C_6H_4\text{-}2'\text{-}C_4H_3S)_3]Cl$ ([3]Cl)

Yield: 91 mg; 85%. ^1H NMR (200 MHz, CDCl$_3$, 21 °C): δ = 1.42 (s, 30H, CH_3), 7.16 (dd, $^3J_{H,H}$ = 3.7 Hz, $^3J_{H,H}$ = 4.8 Hz, 3H, CH–Ar), 7.34 (dd, $^4J_{H,H}$ = 0.9 Hz, $^3J_{H,H}$ = 4.8 Hz, 3H, CH–Ar), 7.45 (dd, $^4J_{H,H}$ = 0.9 Hz, $^3J_{H,H}$ = 3.7 Hz, 3H, CH–Ar), 7.65 (d, $^3J_{H,H}$ = 8.2 Hz, 6H, CH-=Ar), 7.84 (d, $^3J_{H,H}$ = 8.2 Hz, 6H, CH–Ar). $^{13}C\{^1H\}$ NMR(50 MHz, CDCl$_3$, 21 °C): δ = 9.20 (CH_3), 98.28 (d, $^2J_{Rh,C}$ = 4.55 Hz, Rh–C–Ar), 124.18 (C–Ar), 126.05 (C–Ar), 128.74 (C–Ar), 131.71 (C–Ar), 132.27 (C–Ar), 134.06 (C–Ar), 135.21 (C–Ar), 143.07 (C–S-Rh). MS (ESI) m/z: 1049 (M^+). Elemental analysis (%) calcd for $C_{50}H_{51}ClRh_2S_6$ (1085.59): C, 55.32; H, 4.74. Found: C, 55.49; H, 4.92%.

3.2.5. $[Rh_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}S\text{-}p\text{-}C_6H_4\text{-}3'\text{-}C_4H_3S)_3]Cl$ ([4]Cl).

Yield: 82 mg; 76%. ^1H NMR (200 MHz, CDCl$_3$, 21 °C): δ = 1.39 (s, 30H, CH_3), 7.42–7.52 (m, 9H, CH–Ar), 7.64 (d, $^3J_{H,H}$ = 8.2 Hz, 6H, CH–Ar), 7.86 (d, $^3J_{H,H}$ = 8.2 Hz, 6H, CH–Ar). $^{13}C\{^1H\}$ NMR(50 MHz, CDCl$_3$, 21 °C): δ = 9.19 (CH_3), 98.16 (d, $^2J_{Rh,C}$ = 6.83 Hz, Rh-C–Ar), 121.37 (C–Ar), 126.12 (C–Ar), 126.73 (C–Ar), 127.11 (C–Ar), 131.33 (C–Ar), 134.04 (C–Ar), 136.37 (C–Ar), 140.99 (C–S-Rh). MS (ESI) m/z: 1049 (M^+). Elemental analysis (%) calcd for $C_{50}H_{51}ClRh_2S_6$ (1085.59): C, 55.32; H, 4.74. Found: C, 55.45; H, 4.89%.

3.3. X-ray crystallographic study

X-ray data for [3][Br] · CHCl$_3$ · C$_6$H$_6$; $C_{57}H_{58}BrCl_3$-Rh$_2$S$_6$, M = 1327.47, monoclinic, $P2_1/n$ (No. 14), a = 14.7022(13), b = 19.4761(12), c = 19.8721(18) Å, β = 79.487(10)°, U = 5594.7(8) Å^3, T = 153 K, Z = 4, μ(Mo Kα) = 1.709 mm^{-1}, 10,807 reflections measured, 3092 unique (R_{int} = 0.2279) which were used in all calculations. The final R and wR (F^2) were 0.0676 and 0.1328, respectively (all data). [4][Br] · 4.5 CHCl$_3$; $C_{109}H_{102}Br_2$-Cl$_{27}$Rh$_4$S$_{12}$, M = 3325.24, monoclinic, $P2_1/n$ (No. 14), a = 27.8892(16), b = 17.5129(9), c = 28.2672(15) Å, β = 92.724(7)°, U = 13790.7(13) Å^3, T = 153 K, Z = 4, μ(Mo Kα) = 1.797 mm^{-1}, 26,873 reflections measured, 19839 unique (R_{int} = 0.0352) which were used in all calculations. The final R and wR (F^2) were 0.0645 and 0.1747, respectively (all data). The data were measured using a Stoe Image Plate Diffraction system equipped with a ϕ circle, using Mo Kα graphite monochromated radiation (λ = 0.71073 Å) with ϕ range 0–180°, increment 1.5° and 1°, 2θ range from 2.0° to 26°, D_{max}–D_{min} = 12.45–0.81 Å. The structures were solved by direct methods using the program SHELXS-97 [36].

The refinement and all further calculations were carried out using SHELXL-97 [37]. The H-atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-square on F^2. Figs. 1 and 2 were drawn with ORTEP [38].

3.4. Electrochemistry and spectroscopic measurements

The electropolymerization and subsequent study of polymer films were performed using EG&GPAR 273 potentiostat, interfaced to a PC computer. The reference electrode was an Ag$^+$/Ag electrode filled with 0.01 M AgNO$_3$ in acetonitrile. The working electrode was a platinum disc with 0.785 mm^2 area. Tetra-n-butylammonium perchlorate was purchased from Fluka (puriss). Acetonitrile (Aldrich, 99.5%) was used as received. All solutions were degassed by bubbling through argon gas for a few minutes prior to electropolymerization and electrochemical measurements.

UV–Vis characterization of complexes was performed using a quartz cell (1 cm optical path) and Cary 500 (Varian) spectrophotometer. Spectra were recorded between 200 and 800 nm.

4. Supplementary data

CCDC-232661 [3][Br] · CHCl$_3$ · C$_6$H$_6$, and 232,660 [4][Br] · 4.5 CHCl$_3$ contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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