

First Star-Like Oligophenylene Molecules Containing a Dinuclear Organometallic Core

Frédéric Chérioux,^{*,[a]} Bruno Therrien,^[a] and Georg Süss-Fink^[a]

Dedicated to Professeur Bernard Laude on the occasion of his 65th birthday

Keywords: Rhodium / Ruthenium / Oligomerization / Oligophenylene

The cationic complexes $\text{Ru}_2[(p\text{-MeC}_6\text{H}_4\text{iPr})_2(p\text{-SC}_6\text{H}_4\text{Br})_3]^+$ and $\text{Rh}_2[(\text{C}_5\text{Me}_5)_2(p\text{-SC}_6\text{H}_4\text{Br})_3]^+$ are available in quantitative yields from the reaction of $p\text{-HSC}_6\text{H}_4\text{Br}$ with $[\text{Ru}(p\text{-MeC}_6\text{H}_4\text{iPr})\text{Cl}_2]_2$ and $[\text{Rh}(\text{C}_5\text{Me}_5)\text{Cl}_2]_2$ respectively. These complexes are found to undergo triple Suzuki coupling with oligophenylene boronic acids to give $[\text{Ru}_2(p\text{-MeC}_6\text{H}_4\text{iPr})_2(p\text{-SC}_6\text{H}_4\text{Br})_3]^+$

and $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2(p\text{-SC}_6\text{H}_4\text{Br})_3]^+$ respectively. The star-like trisbromo complexes are potential precursors for the insertion of dinuclear organometallic entities into the main chain of conjugated molecules.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2003)

Introduction

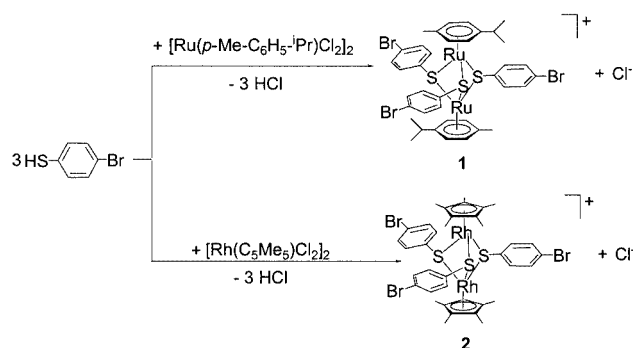
During the two past decades there has been a growing interest in the field of conjugated molecules containing metal centers because of their electronic, nonlinear optical, magnetic and catalytic properties,^[1–3] and more recently for the development of sensors.^[4,5] It is quite impossible to be exhaustive because of the plethora of new compounds synthesized in all these fields of research, but, to the best of our knowledge, all relevant molecules are built around mononuclear building blocks coordinated by different types of organic ligand such as metallocenes, salens, dithiolenes or “nitrogen bridges” (terpyridines, bipyridines or porphyrins). These types of molecules are the most common in the literature because of their extraordinary ability to develop supramolecular structures.^[1,6] However, the challenge remains to develop versatile and selective strategies with a view to creating new molecular designs and new bridging ligands.

Star-shaped molecules can lead to a strong enhancement of the physical properties — such as nonlinear optical susceptibilities^[7,8] or electronic conductivities — in hyperbranched conjugated polymers.^[9] Moreover, there is a large interest in conjugated oligomers for their intrinsic physical properties^[10,11] as because they are model compounds for the study of the corresponding conductive polymers.^[12] In this paper, we report the first example of dinuclear organometallic species in star-like conjugated molecules with sulfur connectivities of the type $[\text{Ru}_2(p\text{-MeC}_6\text{H}_4\text{iPr})_2(p\text{-SC}_6\text{H}_4\text{Br})_3]^+$

and $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2(p\text{-SC}_6\text{H}_4\text{Br})_3]^+$ and the increase of their conjugation length by Suzuki coupling reactions with oligophenylene boronic acids.

Results and Discussion

In accordance with our previous studies,^[13] the dinuclear dichloro complexes $[\text{Ru}(p\text{-MeC}_6\text{H}_4\text{iPr})\text{Cl}_2]_2$ and $[\text{Rh}(\text{C}_5\text{Me}_5)\text{Cl}_2]_2$ are found to react in ethanol with p -bromothiophenol to give the cationic complexes $[\text{Ru}_2(p\text{-MeC}_6\text{H}_4\text{iPr})_2(p\text{-SC}_6\text{H}_4\text{Br})_3]^+$ (**1**) and $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2(p\text{-SC}_6\text{H}_4\text{Br})_3]^+$ (**2**), respectively, which can be isolated in quantitative yield as the chloride salts (Scheme 1).



Scheme 1. Synthesis of star-like trisbromo complexes **1** and **2**

Both cations **1** and **2** are unambiguously characterized by their MS, IR, ^1H and ^{13}C NMR spectroscopic data as well as by satisfactory elemental analysis data of the chloride salts. These cationic complexes are readily soluble as their chloride salts in alcohols, acetone and chlorinated

^[a] Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, 2007 Neuchâtel, Switzerland
Fax: (internat.) + 41-327/182-511
E-mail: frederic.cheriousx@unine.ch

solvents. Their molecular structures were confirmed by a single-crystal X-ray structure analysis of **[1]Cl** and **[2]Cl**. The cations were found to consist of a closed trigonal bipyramid M_2S_3 framework ($M = Ru$ or Rh), with each ruthenium or rhodium atom being coordinated to an η^6 - $Me-C_6H_4iPr$ or an η^5 - C_5Me_5 ligand, respectively, and each sulfur atom carrying a *p*-bromophenyl group. The molecular structures of **1** and **2** are shown in Figure 1.

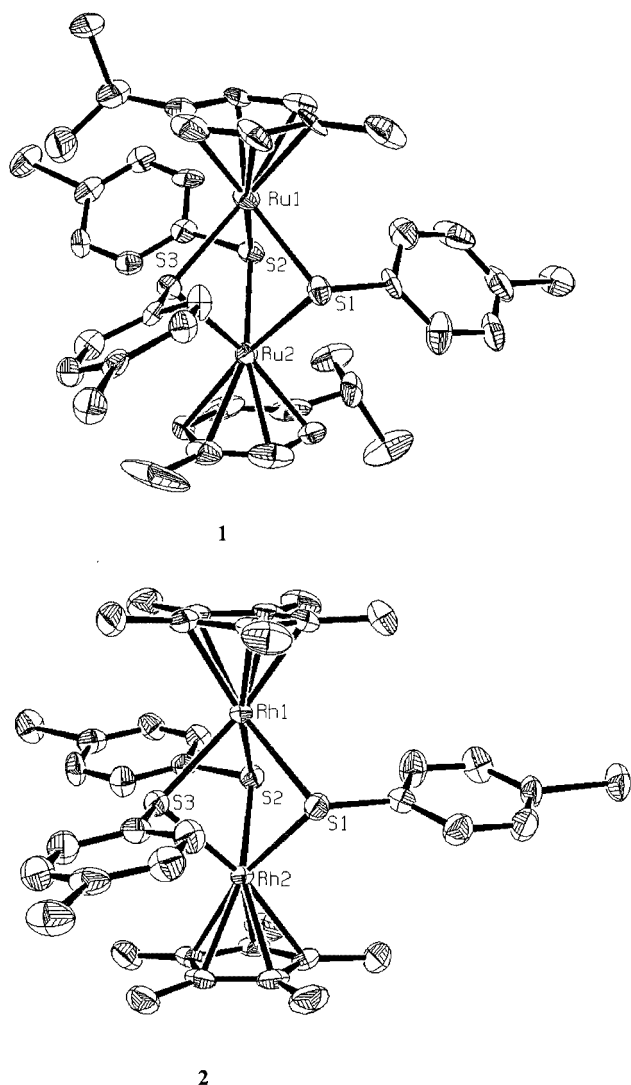
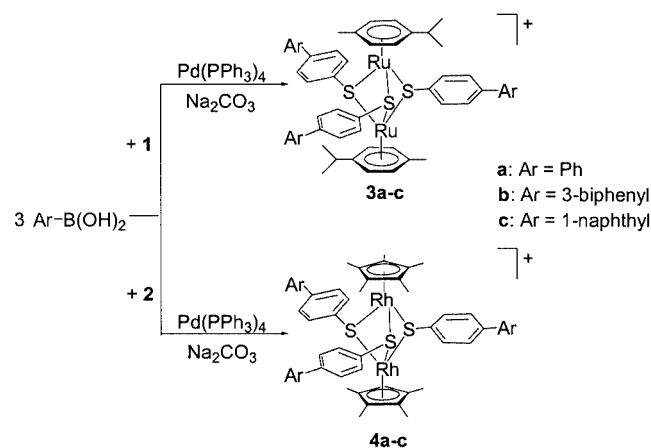


Figure 1. Molecular structure of **[1]Cl** and **[2]Cl**; the chloride ion, solvent molecules, and H atoms have been omitted for clarity; displacement ellipsoids are drawn at the 50% probability level; selected bond lengths (Å) and angles (°): **[1]Cl** Ru(1)–S(1) 2.392(2), Ru(1)–S(2) 2.4192(19), Ru(1)–S(3) 2.385(2), Ru(2)–S(1) 2.411(2), Ru(2)–S(2) 2.3989(19), Ru(2)–S(3) 2.402(2), Ru(1)–Ru(2) 3.3532(8); Ru(1)–S(1)–Ru(2) 88.56(7), Ru(1)–S(2)–Ru(2) 88.20(6), Ru(1)–S(3)–Ru(2) 88.92(8); **[2]Cl** Rh(1)–S(1) 2.3882(16), Rh(1)–S(2) 2.4145(17), Rh(1)–S(3) 2.3937(16), Rh(2)–S(1) 2.4112(17), Rh(2)–S(2) 2.3817(15), Rh(2)–S(3) 2.4059(16), Rh(1)–Rh(2) 3.2254(7); Rh(1)–S(1)–Rh(2) 84.45(5), Rh(1)–S(2)–Rh(2) 84.52(5), Rh(1)–S(3)–Rh(2) 84.44(5)

The bromo-ended star-shaped arrangement adopted by these complexes is very interesting as these compounds represent conductive organometallic nodes. The intramolecular charge transfer (ICT) between the organometallic moieties

and the *p*-bromophenyl groups can be shown by the NMR spectroscopy. An important shielding of the arene (Cp* or *p*- MeC_6H_4iPr) attached to the metal centers is observed in the NMR spectra, whereas a large deshielding of the signals of the *p*-bromophenyl groups is observed in the corresponding NMR spectra (see Exp. Sect.). This phenomenon is larger in the case of ruthenium-based complexes than in the rhodium derivatives. This is proof of the ICT between the *p*-bromophenyl group and the arene moieties through the sulfur bridges and the metal centers in cations **1** and **2**. The bromo sites at the periphery can lead to the insertion of original conductive nodes in the main chain of conjugated oligomers by organometallic cross-coupling Suzuki reactions^[14] with appropriate boronic acid derivatives.

Cations **1** and **2** are found to react with boronic acids (a: phenylboronic acid; b: 3-biphenylboronic acid; c: 1-naphthylboronic acid) in ethanol with $Pd^0(PPh_3)_4$ as catalyst to give the star-shaped conjugated oligomers **3** and **4**, respectively, with yields ranging from 75 to 85% (See Scheme 2). We observed only the formation of the trisubstituted compounds.



Scheme 2. Synthesis of star-shaped conjugated complexes **3** and **4**

Cations **3** and **4** were characterized by their MS and spectroscopic data (IR, 1H and ^{13}C NMR) as well as by satisfactory elemental analysis data of the chloride salts. These cationic complexes are very soluble in alcohols, acetone and chlorinated solvents but not in water. The molecular structure of **4a** was confirmed by a single-crystal X-ray structure analysis of the PF_6 salt. The cation maintains the closed trigonal bipyramid M_2S_3 framework of its precursor **2**, as shown in Figure 2.

Consequently, the insertion of star-shaped dinuclear organometallic nodes into the main chain of a conjugated polymer during their growth is possible via Suzuki cross coupling reactions. These cations can be considered as star-shaped conductive reticulating agents for conjugated oligomers or polymers like 1,3,5-tribromobenzene and its derivatives^[9,15]

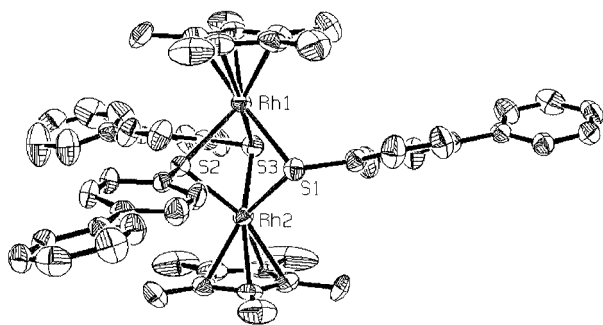


Figure 2. Molecular structure of $[4a]PF_6$; hexafluorophosphate, solvent molecules, and H atoms have been omitted for clarity; displacement ellipsoids are drawn at the 50% probability level; selected bond lengths (Å) and angles ($^\circ$): Rh(1)–S(1) 2.4113(15), Rh(1)–S(2) 2.4006(15), Rh(1)–S(3) 2.4064(15), Rh(2)–S(1) 2.3835(14), Rh(2)–S(2) 2.3840(14), Rh(2)–S(3) 2.4121(17), Rh(1)–Rh(2) 3.2124(6); Rh(1)–S(1)–Rh(2) 84.13(5), Rh(1)–S(2)–Rh(2) 84.35(5), Rh(1)–S(3)–Rh(2) 83.63(5)

Conclusion

In conclusion, we report here the first synthesis of star-shaped dinuclear organometallic entities, based on a closed trigonal bipyramid M_2S_3 framework ($M = Ru$ or Rh). We have demonstrated that these frameworks are conductive nodes that ensure the electronic connectivity of the *p*-bromophenyl group and the arene moieties through the three sulfur bridges and the two metal centers. Cations **1** and **2** react with oligophenylene boronic acid derivatives to give original star-shaped dinuclear organometallic complexes possessing three oligophenylene moieties. The electrochemical behavior, the electronic and optical properties of these conjugated star-shaped oligomers, as well as their insertion into the main chain of conductive polymers, are currently being investigated.

Experimental Section

General Remarks: All reactions were carried out under nitrogen, by using standard Schlenk techniques. Solvents were degassed prior to use. The dinuclear dichloro complexes $[Ru(p\text{-MeC}_6\text{H}_4\text{iPr})Cl_2]_2$ and $[Rh(C_5Me_5)Cl_2]_2$ were synthesized by previously described methods.^[16–18] All other reagents were purchased (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 and TMS. 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).

General Method for the Preparation of **1 and **2**:** The dinuclear dichloro complex $[Ru(p\text{-MeC}_6\text{H}_4\text{iPr})Cl_2]_2$ (60 mg, 0.1 mmol) or $[Rh(C_5Me_5)Cl_2]_2$ (62 mg, 0.1 mmol) was refluxed in technical grade ethanol (25 mL). When the complex had completely dissolved, a solution of *p*-bromothiophenol (95 mg, 0.5 mmol) in 5 mL of ethanol was added dropwise to the hot solution. The resulting mixture was refluxed in ethanol for 3 hours. After cooling to 20 $^\circ\text{C}$, 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 5:1; r_f close to 0.8). Cations **1** and **2** were isolated in the form of their chloride salts, after evaporation of the solvent, as red-orange powders in quantitative yields.

$[Ru_2(p\text{-Me-C}_6\text{H}_4\text{iPr})_2(p\text{-SC}_6\text{H}_4\text{Br})_3]^+$ (1**):** Yield: 107 mg; quantitative. ^1H NMR (200 MHz, CDCl_3 , 21 $^\circ\text{C}$): δ = 0.82 [d, $^3J_{\text{H,H}}$ = 7.0 Hz, 6 H, $(\text{CH}_3)_2\text{CH}$], 0.92 [d, $^3J_{\text{H,H}}$ = 7.0 Hz, 6 H, $(\text{CH}_3)_2\text{CH}$], 1.64 (s, 6 H, CH_3), 1.97 (sept, $^3J_{\text{H,H}}$ = 7.0 Hz, 2 H, $(\text{CH}_3)_2\text{CH}$], 5.23 (d, $^3J_{\text{H,H}}$ = 6.2 Hz, 2 H, CH-Ar), 5.26 (d, $^3J_{\text{H,H}}$ = 5.9 Hz, 2 H, CH-Ar), 5.32 (d, $^3J_{\text{H,H}}$ = 5.9 Hz, 2 H, CH-Ar), 5.60 (d, $^3J_{\text{H,H}}$ = 6.2 Hz, 2 H, CH-Ar), 7.54 (d, $^3J_{\text{H,H}}$ = 8.8 Hz, 6 H, CH-Ar), 7.86 (d, $^3J_{\text{H,H}}$ = 8.8 Hz, 6 H, CH-Ar) ppm. ^{13}C NMR (50 MHz, CDCl_3 , 21 $^\circ\text{C}$): δ = 18.09 (CH_3), 22.12 [$(\text{CH}_3)_2\text{CH}$], 22.94 [$(\text{CH}_3)_2\text{CH}$], 30.00 [$(\text{CH}_3)_2\text{CH}$], 84.12 (Ru-C-Ar), 85.50 (Ru-C-Ar), 85.96 (Ru-C-Ar), 100.29 (Ru-C-Ar), 108.00 (Ru-C-Ar), 123.01 (C-Br), 132.60 (C-Ar), 134.61 (C-Ar), 137.16 (C-S) ppm. MS (ESI): m/z = 1036 $[\text{M}^+]$. $\text{C}_{38}\text{H}_{40}\text{Br}_3\text{ClRu}_2\text{S}_3$ (1070.23): calcd. C 42.65, H 3.77; found C 42.39, H 4.02.

$[Rh_2(C_5Me_5)_2(p\text{-SC}_6\text{H}_4\text{Br})_3]^+$ (2**):** Yield: 107 mg; quantitative. ^1H NMR (200 MHz, CDCl_3 , 21 $^\circ\text{C}$): δ = 1.37 (s, 30 H, CH_3), 7.49 (d, $^3J_{\text{H,H}}$ = 8.4 Hz, 6 H, CH-Ar), 7.66 (d, $^3J_{\text{H,H}}$ = 8.4 Hz, 6 H, CH-Ar) ppm. ^{13}C NMR (50 MHz, CDCl_3 , 21 $^\circ\text{C}$): δ = 8.99 (CH_3), 98.51 (d, $^2J_{\text{Rh,C}}$ = 6.8 Hz; Rh-C-Ar), 123.74 (C-Br), 131.77 (C-Ar), 132.31 (C-Ar), 134.88 (C-S) ppm. MS (ESI): m/z : 1040 $[\text{M}^+]$. $\text{C}_{38}\text{H}_{42}\text{Br}_3\text{ClRh}_2\text{S}_3$ (1075.91): calcd. C 42.30, H 4.20; found C 42.18, H 4.33.

General Method for the Preparation of **3 and **4**:** The trisbromo dinuclear complex $[Ru_2(p\text{-MeC}_6\text{H}_4\text{iPr})_2(p\text{-SC}_6\text{H}_4\text{Br})_3]\text{Cl}$ (107 mg, 0.1 mmol) or $[Rh_2(C_5Me_5)_2(p\text{-SC}_6\text{H}_4\text{Br})_3]\text{Cl}$ (108 mg, 0.1 mmol) and boronic acid derivatives $\text{C}_6\text{H}_5\text{-B(OH)}_2$ (**a**; 40 mg, 0.33 mmol), $\text{C}_{12}\text{H}_9\text{-B(OH)}_2$ (**b**; 65 mg, 0.33 mmol), and $\text{C}_{10}\text{H}_7\text{-B(OH)}_2$ (**c**; 57 mg, 0.33 mmol), were dissolved in technical grade ethanol. Then, an aqueous solution of Na_2CO_3 (1 mL, 2 N), and $\text{Pd(PPh}_3)_4$ catalyst (0.01 mmol, 11 mg) was added. The resulting mixture was refluxed in ethanol for 48 hours. After cooling to 20 $^\circ\text{C}$, 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). Cations **3** and **4** were isolated in the form of their chloride salts, after evaporation of the solvent, as red-orange powders.

$[Ru_2(p\text{-MeC}_6\text{H}_4\text{iPr})_2(p\text{-SC}_6\text{H}_4\text{C}_6\text{H}_5)_3]^+$ (3a**):** Yield: 90 mg; 85%. ^1H NMR (200 MHz, CDCl_3 , 21 $^\circ\text{C}$): δ = 0.81 [d, $^3J_{\text{H,H}}$ = 7.0 Hz, 6 H, $(\text{CH}_3)_2\text{CH}$], 0.92 [d, $^3J_{\text{H,H}}$ = 7.0 Hz, 6 H, $(\text{CH}_3)_2\text{CH}$], 1.70 (s, 6 H, CH_3), 2.03 (sept, $^3J_{\text{H,H}}$ = 7.0 Hz, 2 H, $(\text{CH}_3)_2\text{CH}$], 5.21 (d, $^3J_{\text{H,H}}$ = 5.9 Hz, 2 H, CH-Ar), 5.29 (d, $^3J_{\text{H,H}}$ = 5.9 Hz, 2 H, CH-Ar), 5.33 (d, $^3J_{\text{H,H}}$ = 5.9 Hz, 2 H, CH-Ar), 5.58 (d, $^3J_{\text{H,H}}$ = 5.9 Hz, 2 H, CH-Ar), 7.40–7.54 (m, 9 H, CH-Ar), 7.68 (d, 12 H, $^3J_{\text{H,H}}$ = 8.4 Hz, CH-Ar), 8.05 (d, $^3J_{\text{H,H}}$ = 8.4 Hz, 6 H, CH-Ar) ppm. ^{13}C NMR (50 MHz, CDCl_3 , 21 $^\circ\text{C}$): δ = 18.14 (CH_3), 22.22 [$(\text{CH}_3)_2\text{CH}$], 22.90 [$(\text{CH}_3)_2\text{CH}$], 30.90 [$(\text{CH}_3)_2\text{CH}$], 84.14 (Ru-C-Ar), 85.08 (Ru-C-Ar), 85.58 (Ru-C-Ar), 85.66 (Ru-C-Ar), 100.31 (Ru-C-Ar), 107.55 (Ru-C-Ar), 127.19 (C-Ar), 127.91 (C-Ar), 129.28 (C-Ar), 133.43 (C-Ar), 137.24 (C-Ar), 140.04 (C-Ar), 141.31 (C-S) ppm. MS (ESI): m/z = 1027 $[\text{M}^+]$. $\text{C}_{56}\text{H}_{55}\text{ClRu}_2\text{S}_3$ (1061.83): calcd. C 63.34, H 5.22; found C 63.05, H 5.05.

$[Ru_2(p\text{-MeC}_6\text{H}_4\text{iPr})_2(p\text{-SC}_6\text{H}_4(m\text{-C}_6\text{H}_4\text{C}_6\text{H}_5))_3]^+$ (3b**):** Yield: 110 mg; 85%. ^1H NMR (200 MHz, CDCl_3 , 21 $^\circ\text{C}$): δ = 0.82 [d, $^3J_{\text{H,H}}$ = 7.0 Hz, 6 H, $(\text{CH}_3)_2\text{CH}$], 0.93 [d, $^3J_{\text{H,H}}$ = 7.0 Hz, 6 H, $(\text{CH}_3)_2\text{CH}$], 1.71 (s, 6 H, CH_3), 2.03 (sept, $^3J_{\text{H,H}}$ = 7.0 Hz, 2 H, $(\text{CH}_3)_2\text{CH}$], 5.24 (d, $^3J_{\text{H,H}}$ = 5.9 Hz, 2 H, CH-Ar), 5.31 (d, $^3J_{\text{H,H}}$ =

5.9 Hz, 2 H, *CH*-Ar), 5.36 (d, $^3J_{\text{H,H}} = 5.9$ Hz, 2 H, *CH*-Ar), 5.60 (d, $^3J_{\text{H,H}} = 5.9$ Hz, 2 H, *CH*-Ar), 7.40–7.76 (m, 30 H, *CH*-Ar), 7.89 (s, 3 H, *CH*-Ar), 8.09 (d, $^3J_{\text{H,H}} = 8.1$ Hz, 6 H, *CH*-Ar) ppm. ^{13}C NMR (50 MHz, CDCl_3 , 21 °C): $\delta = 18.14$ (CH_3), 22.19 [$(\text{CH}_3)_2\text{CH}$], 22.95 [$(\text{CH}_3)_2\text{CH}$], 30.90 [$(\text{CH}_3)_2\text{CH}$], 84.12 (Ru-*C*-Ar), 85.01 (Ru-*C*-Ar), 85.55 (Ru-*C*-Ar), 85.63 (Ru-*C*-Ar), 100.25 (Ru-*C*-Ar), 107.67 (Ru-*C*-Ar), 126.94 (*C*-Ar), 127.56 (*C*-Ar), 127.85 (*C*-Ar), 128.04 (*C*-Ar), 129.17 (*C*-Ar), 129.76 (*C*-Ar), 133.52 (*C*-Ar), 137.48 (*C*-Ar), 140.60 (*C*-Ar), 141.25 (*C*-Ar), 142.28 (*C*-S) ppm. MS (ESI): $m/z = 1255$ [M^+]. $\text{C}_{74}\text{H}_{67}\text{ClRu}_2\text{S}_3$ (1290.11): calcd. C 68.89, H 5.23, found C 68.65, H 5.35.

[Ru₂(*p*-Me-C₆H₄-*i*Pr)₂(*p*-SC₆H₄C₁₀H₇)₃]⁺ (3c): Yield: 100 mg; 85%. ^1H NMR (200 MHz, CDCl_3 , 21 °C): $\delta = 0.92$ [d, $^3J_{\text{H,H}} = 7.0$ Hz, 6 H, (CH_3)₂CH], 1.05 [d, $^3J_{\text{H,H}} = 7.0$ Hz, 6 H, (CH_3)₂CH], 1.86 (s, 6 H, CH_3), 2.13 (sept, $^3J_{\text{H,H}} = 7.0$ Hz, 2 H, (CH_3)₂CH], 5.32 (d, $^3J_{\text{H,H}} = 5.9$ Hz, 2 H, *CH*-Ar), 5.40 (d, $^3J_{\text{H,H}} = 5.9$ Hz, 2 H, *CH*-Ar), 5.44 (d, $^3J_{\text{H,H}} = 5.9$ Hz, 2 H, *CH*-Ar), 5.71 (d, $^3J_{\text{H,H}} = 5.9$ Hz, 2 H, *CH*-Ar), 7.51–7.62 (m, 21 H, *CH*-Ar), 7.93 (d, $^3J_{\text{H,H}} = 8.1$ Hz, 6 H, *CH*-Ar), 8.14 (d, $^3J_{\text{H,H}} = 8.1$ Hz, 6 H, *CH*-Ar) ppm. ^{13}C NMR (50 MHz, CDCl_3 , 21 °C): $\delta = 18.29$ (CH_3), 22.54 [$(\text{CH}_3)_2\text{CH}$], 22.83 [$(\text{CH}_3)_2\text{CH}$], 30.95 [$(\text{CH}_3)_2\text{CH}$], 84.46 (Ru-*C*-Ar), 84.73 (Ru-*C*-Ar), 85.17 (Ru-*C*-Ar), 85.52 (Ru-*C*-Ar), 101.03 (Ru-*C*-Ar), 106.98 (Ru-*C*-Ar), 125.75 (*C*-Ar), 126.26 (*C*-Ar), 126.62 (*C*-Ar), 127.35 (*C*-Ar), 128.43 (*C*-Ar), 128.81 (*C*-Ar), 131.10 (*C*-Ar), 131.51 (*C*-Ar), 132.95 (*C*-Ar), 134.15 (*C*-Ar), 137.20 (*C*-Ar), 139.22 (*C*-Ar), 141.24 (*C*-S) ppm. MS (ESI): $m/z = 1177$ [M^+]. $\text{C}_{68}\text{H}_{61}\text{ClRu}_2\text{S}_3$ (1212.00): calcd. C 67.39, H 5.07, found C 67.68, H 4.91.

[Rh₂(C₅Me₅)₂(*p*-SC₆H₄C₆H₅)₃]⁺ (4a): Yield: 90 mg; 75%. ^1H NMR (200 MHz, CDCl_3 , 21 °C): $\delta = 1.37$ (s, 30 H, CH_3), 7.41–7.55 (m, 9 H, *CH*-Ar), 7.65 (d, $^3J_{\text{H,H}} = 8.4$ Hz, 6 H, *CH*-Ar), 7.71 (d, $^3J_{\text{H,H}} = 8.1$ Hz, 6 H, *CH*-Ar), 7.92 (d, $^3J_{\text{H,H}} = 8.1$ Hz, 6 H, *CH*-Ar) ppm. ^{13}C NMR (50 MHz, CDCl_3 , 21 °C): $\delta = 9.05$ (CH_3), 98.20 (d, $^2J_{\text{Rh,C}} = 7.58$ Hz, Rh-*C*-Ar), 127.08 (*C*-Ar), 127.40 (*C*-Ar), 128.23 (*C*-Ar), 129.30 (*C*-Ar), 131.97 (*C*-Ar), 134.01 (*C*-Ar), 139.75 (*C*-S) ppm. MS (ESI): $m/z = 1031$ [M^+]. $\text{C}_{56}\text{H}_{57}\text{ClRh}_2\text{S}_3$ (1067.51): calcd. C 63.01, H 5.38, found C 62.76, H 5.52.

[Rh₂(C₅Me₅)₂(*p*-SC₆H₄(*m*-C₆H₄C₆H₅))₃]⁺ (4b): Yield: 97 mg; 75%. ^1H NMR (200 MHz, CDCl_3 , 21 °C): $\delta = 1.44$ (s, 30 H, CH_3), 7.41–7.77 (m, 30 H, *CH*-Ar), 7.89 (s, 3 H, *CH*-Ar), 7.95 (d, $^3J_{\text{H,H}} = 8.42$ Hz, 6 H, *CH*-Ar) ppm. ^{13}C NMR (50 MHz, CDCl_3 , 21 °C): $\delta = 9.05$ (CH_3), 98.27 (d, $^2J_{\text{Rh,C}} = 5.3$ Hz, Rh-*C*-Ar), 126.01 (*C*-Ar), 127.11 (*C*-Ar), 127.88 (*C*-Ar), 128.67 (*C*-Ar), 129.79 (*C*-Ar), 132.04 (*C*-Ar), 134.04 (*C*-Ar), 140.19 (*C*-Ar), 141.19 (*C*-Ar), 141.69 (*C*-Ar), 142.39 (*C*-S) ppm. MS (ESI): $m/z = 1259$ [M^+]. $\text{C}_{74}\text{H}_{69}\text{ClRh}_2\text{S}_3$ (1295.80): calcd. C 68.59, H 5.37, found C 68.75, H 5.09.

[Rh₂(C₅Me₅)₂(*p*-SC₆H₄C₁₀H₇)₃]⁺ (4c): Yield: 91 mg; 75%. ^1H NMR (200 MHz, CDCl_3 , 21 °C): $\delta = 1.47$ (s, 30 H, CH_3), 7.51–7.65 (m, 21 H, *CH*-Ar), 7.81 (d, $^3J_{\text{H,H}} = 8.1$ Hz, 6 H, *CH*-Ar), 8.01 (d, $^3J_{\text{H,H}} = 8.1$ Hz, 6 H, *CH*-Ar) ppm. ^{13}C NMR (50 MHz, CDCl_3 , 21 °C): $\delta = 9.05$ (CH_3), 98.13 (d, $^2J_{\text{Rh,C}} = 5.5$ Hz, Rh-*C*-Ar), 125.79 (*C*-Ar), 126.11 (*C*-Ar), 126.94 (*C*-Ar), 127.31 (*C*-Ar), 128.49 (*C*-Ar), 128.71 (*C*-Ar), 131.34 (*C*-Ar), 131.82 (*C*-Ar), 132.59 (*C*-Ar), 134.32 (*C*-Ar), 137.24 (*C*-Ar), 139.53 (*C*-Ar), 142.28 (*C*-S) ppm. MS (ESI): $m/z = 1181$ [M^+]. $\text{C}_{68}\text{H}_{63}\text{ClRh}_2\text{S}_3$ (1217.69): calcd. C 67.07, H 5.21, found C 67.39, H 4.97.

X-ray Crystallographic Study

[I]Cl·CHCl₃: $\text{C}_{39}\text{H}_{41}\text{Br}_3\text{Cl}_4\text{Ru}_2\text{S}_3$, $M = 1189.57$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 10.7690(6)$, $b = 15.0037(8)$, $c = 26.6643(16)$ Å, $U = 4308.3(4)$ Å³, $T = 153$ K, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 3.905$ mm^{−1},

8018 reflections measured, 5392 unique ($R_{\text{int}} = 0.0719$) which were used in all calculations. The final wR (F^2) was 0.0827 (all data).

[2]Cl·3CHCl₃·0.5C₆H₆: $\text{C}_{44}\text{H}_{48}\text{Br}_3\text{Cl}_{10}\text{Rh}_2\text{S}_3$, $M = 1473.05$, monoclinic, $P2_1/n$ (no. 14), $a = 14.0257(11)$, $b = 24.8541(13)$, $c = 15.9642(13)$ Å, $\beta = 92.495(10)^\circ$, $U = 5559.8(7)$ Å³, $T = 153$ K, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 3.374$ mm^{−1}, 10607 reflections measured, 8186 unique ($R_{\text{int}} = 0.0433$) which were used in all calculations. The final wR (F^2) was 0.1567 (all data).

[4a]PF₆·2C₆H₆: $\text{C}_{68}\text{H}_{69}\text{F}_6\text{PRh}_2\text{S}_3$, $M = 1333.20$, monoclinic, $P2_1/c$ (no. 14), $a = 19.5028(10)$, $b = 15.0341(9)$, $c = 22.5937(14)$ Å, $\beta = 96.209(7)^\circ$, $U = 6585.8(7)$ Å³, $T = 153$ K, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 0.675$ mm^{−1}, 12536 reflections measured, 6576 unique ($R_{\text{int}} = 0.0845$) which were used in all calculations. The final wR (F^2) was 0.1191 (all data).

he data were measured using a Stoe Image Plate Diffraction system equipped with a ϕ circle, using Mo- $K\alpha$ graphite monochromated radiation ($\lambda = 0.71073$ Å) with ϕ range 0–180°, increment 1°, 2 θ range from 2.0–26°, $D_{\text{max}}-D_{\text{min}} = 12.45-0.81$ Å. The structures were solved by direct methods using 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 using the SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-square on F^2 .

CCDC-197151 ([I]Cl·CHCl₃), CCDC-197152 ([2]Cl·3CHCl₃·0.5C₆H₆) and CCDC-197153 ([4a]PF₆·2C₆H₆) contain the supplementary crystallographic data for this paper. 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].

Acknowledgments

Financial support of the Fond National Suisse de la Recherche Scientifique is gratefully acknowledged. The authors are also indebted to the Johnson Matthey Technology Centre for a loan of ruthenium trichloride hydrate.

- [1] J.-M. Lehn, *Supramolecular Chemistry, Concepts and Perspectives*, VCH, Weinheim, 1995.
- [2] R. Ziessel, L. Charbonnière, M. Cesario, T. Prangé, H. Nierengarten, *Angew. Chem. Int. Ed.* **2002**, *41*, 975–979.
- [3] K. Sénéchal, O. Maury, H. le Bozec, I. Ledoux, J. Zyss, *J. Am. Chem. Soc.* **2002**, *124*, 4560–4561.
- [4] K. K.-W. Lo, W.-K. Hui, D. Chung-Ming Ng, *J. Am. Chem. Soc.* **2002**, *124*, 9344–9345.
- [5] D. T. MacQuade, A. E. Pullen, T. M. Swager, *Chem. Rev.* **2000**, *100*, 2537–2574.
- [6] U. S. Schubert, C. Eschbaumer, *Angew. Chem. Int. Ed.* **2002**, *41*, 2892–2926. and ref. therein.
- [7] J. Zyss, I. Ledoux, *Chem. Rev.* **1994**, *94*, 77–105.
- [8] C. Dhenault, I. Ledoux, I. D. W. Samuel, M. Bourgaunt, H. Le Bozec, *Nature* **1995**, *374*, 339–342.
- [9] F. Chérioux, L. Guyard, *Adv. Func. Mater.* **2001**, *11*, 305–309.
- [10] R. Anémian, J.-C. Mulatier, C. Andraud, O. Stephan, J.-C. Vial, *Chem. Commun.* **2002**, 1608–1609.
- [11] *Electronic Materials: The Oligomer Approach* (Eds.: K. Müllen and G. Wegner), Wiley VCH, Weinheim, 1998.
- [12] L. L. Miller, Y. Yu, *J. Org. Chem.* **1995**, *60*, 6813–6819 and references cited therein.
- [13] F. Chérioux, C. M. Thomas, B. Therrien, G. Süß-Fink, *Chem. Eur. J.* **2002**, *8*, 4377–4382.

- [14] N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, 95, 2457–2483.
- [15] J. Pang, Y. Tao, S. Freiberg, X.-P. Yang, M. D'Iorio, S. Wang, *J. Mater. Chem.* **2002**, 12, 206–212 and references cited therein.
- [16] R. A. Zelonka, M. C. Baird, *Can. J. Chem.* **1972**, 50, 3063–3068.
- [17] J. W. Wang, K. Moseley, P. M. Maitlis, *J. Am. Chem. Soc.* **1969**, 91, 5970–5977.
- [18] M. A. Bennett, A. K. Smith, *J. Chem. Soc., Dalton Trans.* **1974**, 233–241.
- [19] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, 46, 467.
- [20] G. M. Sheldrick, SHELXL-97. University of Göttingen, Göttingen, Germany, **1999**.

Received November 28, 2002
[I02655]