

Specific reactivity of SH versus OH functions towards dinuclear arene ruthenium units: synthesis of cationic complexes of the type $[(\text{arene})_2\text{Ru}_2(\text{SR})_3]^+$

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Abstract

The reaction of $[(\text{arene})\text{RuCl}_2]_2$ (arene = C_6H_6 , $p\text{-Me-C}_6\text{H}_4\text{-}^i\text{Pr}$, C_6Me_6) with p -thiocresol, 2-mercaptoethanol and p -mercaptophenol in refluxing ethanol gives the tris-thiolato complexes $[(\text{arene})_2\text{Ru}_2(\text{SR})_3]^+$ ($\text{R} = p\text{-C}_6\text{H}_4\text{-Me}$, $\text{CH}_2\text{CH}_2\text{OH}$, $p\text{-C}_6\text{H}_4\text{OH}$) which can be isolated as the chloride salts. The remarkable selectivity of (arene)ruthenium units for SH versus OH functions reflects the affinity of ruthenium towards sulfur.

Keywords: Multi-functional ligand; (Arene)ruthenium; Tristhiolato; Mercaptophenol

1. Introduction

The two past decades have witnessed a steadily growing interest in the chemistry of dendrimers, a new class of macromolecules that can be considered as monodisperse, precisely ordered, polyfunctional polymers [1]. Nowadays a large variety of metallodendrimers is now accessible. Even though the molecular design of metallodendrimers seems to be without limits, it is restricted to one type of metal either in the periphery or in the core. There are few reports on the incorporation of metal complexes into the dendron arms [2] even with different metal atoms [3], but these examples are rare. In most cases, the synthesis of metallodendrimers built around a metal core is based on ligand exchange of an organometallic precursor by the corresponding organic dendrons, but it appears quite impossible to insert a metal atom during the growth of the dendrimer generation, because there is a competition between the ligand exchange leading to the next generation and the ligand exchange of the previous generation. This effect represents the main problem of the synthesis of poly-

metallic dendrimers. A solution to overcome this problem consists in elaborating a specific reaction between one metal centre and a bifunctional ligand, in order to develop new organometallic entities which are able to grow in dendritic molecules and possess free sites for another metal complexation. To the best of our knowledge, there is only one report in the literature of this type of approach [3].

In this paper, we report on a convenient reaction that leads to the formation of multifunctional organometallogendrimer precursors, which can play the same role as polyphenols play in the development of purely organic dendrimers [1b]. Our starting idea is based on previous work concerning the reactivity of thiols versus dinuclear ruthenium entities: the synthesis of pentamethylcyclopentadienylruthenium tristhiolato complexes has been reported by Hidaï and coworkers [4] This reaction to give $[(\text{C}_5\text{Me}_5)_2\text{Ru}_2(\text{SAr})_3]\text{Cl}$ takes place in anhydrous dichloromethane using $[(\text{C}_5\text{Me}_5)\text{RuCl}_2]_2$ and the corresponding aromatic mercaptans [4a] or in methanol using $[(\text{C}_5\text{Me}_5)\text{RuCl}_2]_2$ and the sodium salt of the corresponding aromatic mercaptans [4b]. This reaction prompted us to suppose that also arene ruthenium derivatives can react specifically with thiols in alcohol solution, because the formation of the oxo analogues $[(\text{C}_5\text{Me}_5)_2\text{Ru}_2(\text{OAr})_3]\text{Cl}$ as minor products has not been reported

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[4b]. Herein, we report a convenient synthetic approach to develop multi-functional molecules based on dinuclear arene-ruthenium units with the ability to fix organic functions at their periphery.

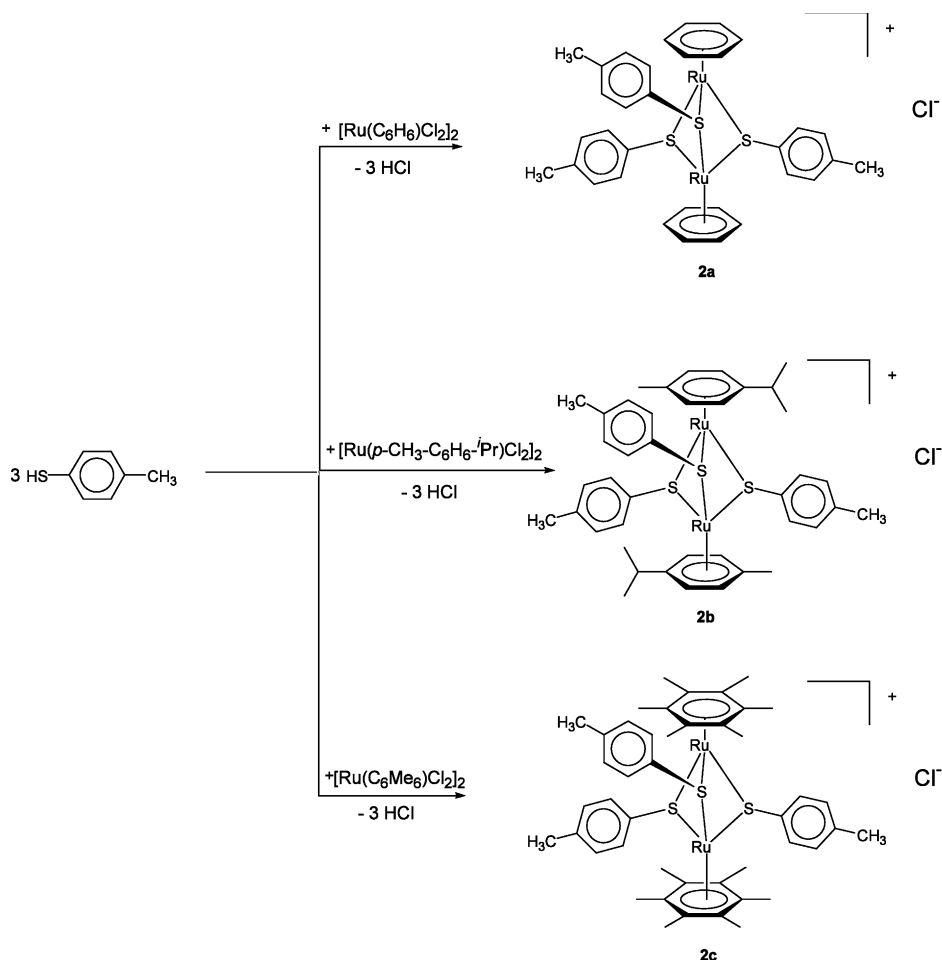
2. Results and discussion

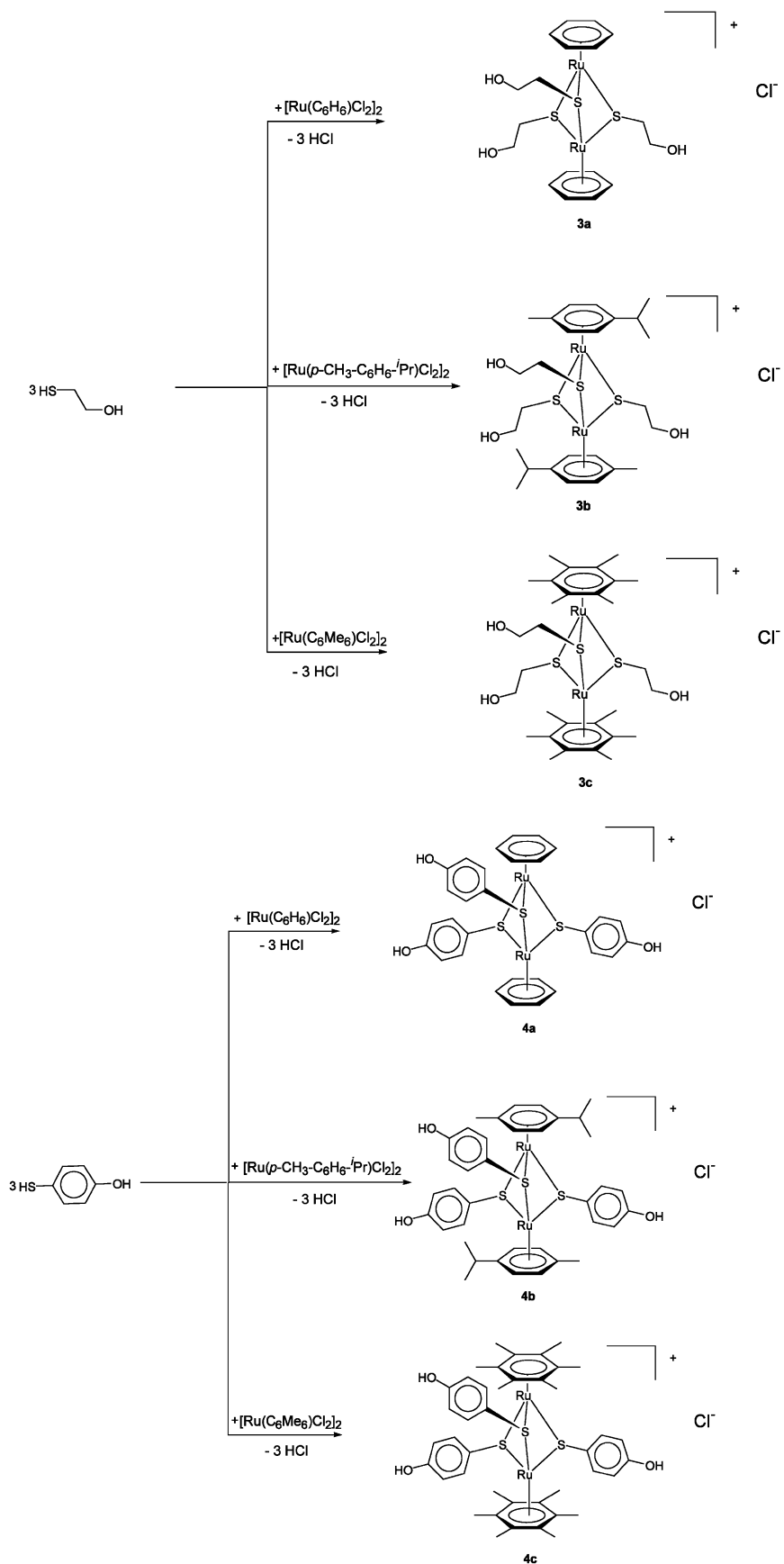
With the aim to check the specific reaction of [(arene)RuCl₂]₂ with SH and not with OH functions, we have adopted the following experimental set-up: a solution of 1 equiv. of arene ruthenium compounds **1** (100 mg close to 0.2 mmol, **1a**, [Ru₂(C₆H₆)₂Cl₂]₂; **1b**, [Ru₂(*p*-CH₃-C₆H₄-^{*i*}Pr)₂Cl₂]₂; **1c**, [Ru₂(C₆Me₆)₂Cl₂]₂) in ethanol (400 mmol, 25 ml) and 4 equiv. of *p*-thiocresol (100 mg, 0.8 mmol) is refluxed overnight in air to give the products **2** (Scheme 1).

The remarkable preference for the SH function of the *p*-thiocresol versus the OH function of the solvent by the dinuclear ruthenium units reflects the molecular affinity of sulfur towards this metal: the reaction is carried out in ethanol with an ethanol/*p*-thiocresol ratio of 2000:1, and no trace of diruthenium complexes

containing oxo bridging ligands is detected. This specificity in the SH/OH competition can be used as the key for the synthesis of multifunctional compounds. In fact, if arene ruthenium derivatives are able to recognize sulfur atoms in an alcoholic solution, it may be possible to use a bi-functional mercapto-alcohol instead of thiols and, consequently, the resulting products would possess only free hydroxy functions and thiolato bridges. We have chosen 2-mercaptoethanol and 4-mercaptophenol as bi-functional molecules, which gives indeed the desired products (Scheme 2).

All products are isolated as orange-red powders by column chromatography, and the chloride salts are well soluble in alcohols, DMSO or DMF. The molecular compositions and structures proposed are in accordance with the spectroscopic and analytical data of the chloride salts obtained. In the mass spectra, only the molecular peak is detected without any minor products. The coordination of sulfur (and not of oxygen) can already be concluded from infrared spectra: In the case of *p*-mercaptophenol, the infrared spectrum shows a $\nu_{\text{O-H}}$ frequency close to 3570 cm⁻¹ and a $\nu_{\text{S-H}}$ close to 2680 cm⁻¹. Compounds **4** exhibit only one large band





Scheme 2. Synthesis of $[(\text{arene})_2\text{Ru}_2(\text{S}-\text{C}_2\text{H}_4-\text{OH})_3]\text{Cl}$ (3) and $[(\text{arene})_2\text{Ru}_2(\text{S}-\text{C}_6\text{H}_4-p\text{-OH})_3]\text{Cl}$ (4).

close to 3400 cm^{-1} ($\nu_{\text{O-H}}$), being in good agreement with thiolato bridges ligand and free hydroxy functions.

The ^1H NMR spectra are even more convincing: In the case of the reaction between *p*-mercaptophenol and $[\text{Ru}_2(p\text{-CH}_3\text{-C}_6\text{H}_4\text{-}^i\text{Pr})_2\text{Cl}_2]_2$, the spectrum of the product $[(p\text{-CH}_3\text{-C}_6\text{H}_4\text{-}^i\text{Pr})_2\text{Ru}_2(\text{S-C}_6\text{H}_4\text{-}^p\text{-OH})_3]\text{Cl}$ (spectrum B, Fig. 1) clearly demonstrates that **4b** contains $\mu\text{-SC}_6\text{H}_4\text{OH}$ ligand and free hydroxy functions. According to Pretsch et al. [5] the protons of *p*-mercaptophenol (spectrum A) can be assigned unambiguously. Spectrum B corresponds to the product **4b**: the Hc signal has disappeared, Ha is strongly deshielded (+0.62 ppm), while Hb is quite deshielded (+0.12 ppm), proving the formation of thiolato bridges, in which the sulfur atom is a three-electrons donor ligand. Thus, the electronic density around the sulfur atom is strongly decreasing, leading to a large deshielding of Ha, whereas Hb is less affected by this modification in the electronic structure of the sulfur atom. This effect is observed in all compounds **3** and **4**.

Moreover, the ^1H NMR spectrum of **4b** gives further structural informations: the arene moieties are more strongly shielded (signals at 0.92; 1.65; 2.01; 5.31 ppm, spectrum B) with respect to the starting complex **1b**

(signals at 1.32; 2.22; 2.80; 5.68 and 5.90 ppm, spectrum C). This is due to the stronger electron-donor power of the thiolato bridges with respect to the chloro ligand. On the other hand, the steric hindrance of the $\mu\text{-SC}_6\text{H}_4\text{OH}$ ligands with respect to the isopropyl substituents and the staggered conformation of the complexes leads to a multiplication of the signals of the two *p*-cymene ligands. These effects are also present in the case of **3b** but less pronounced because of the lower steric hindrance of an ethyl chain as compared to a phenyl group.

3. Experimental

The dinuclear dichloro complex have been synthesized by standard methods (**1a**, $[\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2]_2$ **6a**; **1b**, $[\text{Ru}(p\text{-CH}_3\text{-C}_6\text{H}_4\text{-}^i\text{Pr})\text{Cl}_2]_2$ **6b**; **1c**, $[\text{Ru}(\text{C}_6(\text{CH}_3)_6)\text{Cl}_2]_2$ **6b**).

3.1. General method for **2**, **3** and **4**

The dinuclear dichloro complex (0.1 mmol), (**1a**, $[\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2]_2$, 50 mg; **1b**, $[\text{Ru}(p\text{-CH}_3\text{-C}_6\text{H}_4\text{-}^i\text{Pr})\text{Cl}_2]_2$, 61 mg; **1c**, $[\text{Ru}(\text{C}_6(\text{CH}_3)_6)\text{Cl}_2]_2$, 69 mg) is refluxed in 25

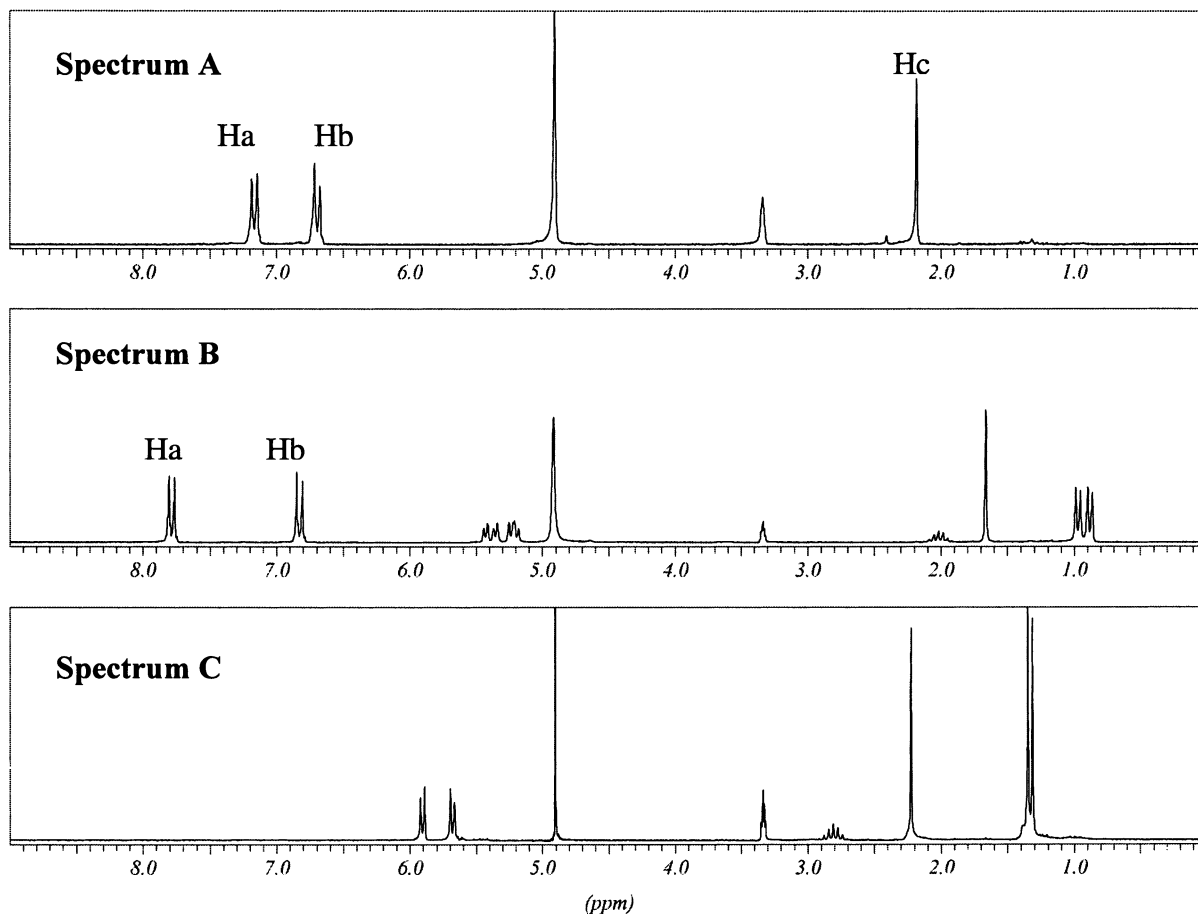


Fig. 1. ^1H NMR spectra of *p*-mercaptophenol (spectrum A), $[\text{Ru}_2(p\text{-CH}_3\text{-C}_6\text{H}_4\text{-}^i\text{Pr})_2\text{Cl}_2]_2$ (spectrum C) and $[(p\text{-CH}_3\text{-C}_6\text{H}_4\text{-}^i\text{Pr})_2\text{Ru}_2(\text{S-C}_6\text{H}_4\text{-}^p\text{-OH})_3]\text{Cl}$ (spectrum B).

ml of technical EtOH. When the complex is completely dissolved, a solution of 0.6 mmol of the thiol (*p*-thiocresol, 75 mg; 2-mercaptoethanol, 47 mg; *p*-mercaptophenol, 76 mg) in 5 ml of EtOH is added drop-wise to the hot solution. The resulting mixture is refluxed in EtOH for 3 h. After cooling to 20 °C, the red solution is filtered, and the solvent is removed under reduced pressure. The oil obtained is purified by column chromatography (silica gel, CH₂Cl₂/EtOH 5:1, *R_f* close to 0.8). Compounds **2**, **3** and **4** are isolated by evaporation of the solvent as red–orange microcrystalline powders in quantitative yields, except in the case of [Ru(C₆H₆)Cl₂]₂ as starting complex (yield: 80%).

3.2. [Ru₂(C₆H₆)₂(S–C₆H₄–*p*-CH₃)₃]Cl (**2a**)

¹H NMR (200 MHz, CDCl₃): δ (ppm) = 7.72 (d, ³*J* = 8.1 Hz, 6H; *H*–*Ar*), 7.21 (d, ³*J* = 8.1 Hz, 6H; *H*–*Ar*), 5.41 (s, 12H; Ru–*benzene*), 2.38 (s, 9H; CH₃). MS (ESI) *m/z*: 729 [*M*+H⁺]. *Anal. Calc.* for C₃₃H₃₃ClRu₂S₃ (763.41): C, 51.92; H, 4.36. Found: C, 51.65; H, 4.51%.

3.3. [Ru₂(*p*-CH₃–C₆H₄–^{*i*}Pr)₂(S–C₆H₄–*p*-CH₃)₃]Cl (**2b**)

¹H NMR (200 MHz, CDCl₃) δ (ppm): 7.73 (d, ³*J* = 8.1 Hz, 6H; *H*–*Ar*), 7.17 (d, ³*J* = 8.1 Hz, 6H; *H*–*Ar*), 5.31 (d, ³*J* = 6.0 Hz, 2H; *H*–*Ar*), 5.18 (d, ³*J* = 5.7 Hz, 2H; *H*–*Ar*), 5.11 (d, ³*J* = 6.0 Hz, 2H; *H*–*Ar*), 5.06 (d, ³*J* = 5.7 Hz, 2H; *H*–*Ar*), 2.36 (9H, s; CH₃), 1.94 (sept, ³*J* = 6.8 Hz, 2H; (CH₃)₂CH), 1.60 (6H, s; CH₃), 0.89 (d, ³*J* = 6.8 Hz, 6H; (CH₃)₂CH), 0.78 (d, ³*J* = 6.8 Hz, 6H; (CH₃)₂CH). MS (ESI) *m/z*: 842 [*M*+H⁺]. *Anal. Calc.* for C₄₁H₄₉ClRu₂S₃ (875.62): C, 56.24; H, 5.64. Found: C, 56.38; H, 5.86%.

3.4. [Ru₂(C₆(CH₃)₆)₂(S–C₆H₄–*p*-CH₃)₃]Cl (**2c**)

¹H NMR (200 MHz, CDCl₃) δ (ppm): 7.77 (d, ³*J* = 8.0 Hz, 6H; *H*–*Ar*), 7.16 (d, ³*J* = 8.0 Hz, 6H; *H*–*Ar*), 2.39 (9H, s; CH₃), 1.71 (36H, s; CH₃). MS (ESI) *m/z*: 897 [*M*+H⁺]. *Anal. Calc.* for C₄₅H₅₇ClRu₂S₃ (931.72): C, 58.01; H, 6.17. Found: C, 57.76; H, 5.98%.

3.5. [Ru₂(C₆H₆)₂(S–C₂H₄–OH)₃]Cl (**3a**)

IR (KBr): $\tilde{\nu}$ = 3405 (OH). ¹H NMR (200 MHz, CD₃OD) δ (ppm): 5.69 (s, 12H; Ru–*benzene*) 3.66 (t, ³*J* = 6.1 Hz, 6H; O–CH₂–CH₂), 2.50 (t, ³*J* = 6.1 Hz, 6H; S–CH₂–CH₂). MS (ESI) *m/z*: 591 [*M*+H⁺]. *Anal. Calc.* for C₁₈H₂₇ClO₃Ru₂S₃ (625.2): C, 34.58; H, 4.35. Found: C, 34.71; H, 4.51%.

3.6. [Ru₂(*p*-CH₃–C₆H₄–^{*i*}Pr)₂(S–C₂H₄–OH)₃]Cl (**3b**)

IR (KBr): $\tilde{\nu}$ = 3405 (OH). ¹H NMR (200 MHz, CD₃OD) δ (ppm): 5.67 (d, ³*J* = 5.9 Hz, 2H; *H*–*Ar*), 5.48 (d, ³*J* = 5.9 Hz, 2H; *H*–*Ar*), 5.42 (d, ³*J* = 5.9 Hz, 4H; *H*–*Ar*), 3.86 (t, ³*J* = 6.1 Hz, 6H; O–CH₂–CH₂), 2.84 (sept, ³*J* = 6.6 Hz, 2H; (CH₃)₂CH), 2.64 (t, ³*J* = 6.1 Hz, 6H; S–CH₂–CH₂), 2.19 (6H, s; CH₃), 1.32 (d, ³*J* = 6.6 Hz, 6H; (CH₃)₂CH), 1.29 (d, ³*J* = 6.6 Hz, 6H; (CH₃)₂CH). MS (ESI) *m/z*: 703 [*M*+H⁺]. *Anal. Calc.* for C₂₆H₄₃ClO₃Ru₂S₃ (737.41): C, 42.35; H, 5.88. Found: C, 42.19; H, 5.69%.

3.7. [Ru₂(C₆(CH₃)₆)₂(S–C₂H₄–OH)₃]Cl (**3c**)

IR (KBr): $\tilde{\nu}$ = 3405 (OH). ¹H NMR (200 MHz, CD₃OD) δ (ppm): 3.66 (t, ³*J* = 6.1 Hz, 6H; O–CH₂–CH₂), 2.50 (s, ³*J* = 6.1 Hz, 6H; S–CH₂–CH₂), 1.59 (36H, s; CH₃). MS (ESI) *m/z*: 759 [*M*+H⁺]. *Anal. Calc.* for C₃₀H₅₁ClO₃Ru₂S₃ (793.51): C, 45.41; H, 6.48. Found: C, 45.29; H, 6.24%.

3.8. [Ru₂(C₆H₆)₂(S–C₆H₄–*p*-OH)₃]Cl (**4a**)

IR (KBr): $\tilde{\nu}$ = 3430 (OH). ¹H NMR (200 MHz, CD₃OD) δ (ppm): 7.72 (d, ³*J* = 8.1 Hz, 6H; *H*–*Ar*), 7.21 (d, ³*J* = 8.1 Hz, 6H; *H*–*Ar*), 5.41 (s, 12H; Ru–*benzene*), ¹³C NMR (50 MHz, [*d*₆]DMSO) δ (ppm): 115.9, 125.4 (Ru–*benzene*), 132.3, 133.6, 144.5. MS (ESI) *m/z*: 736 [*M*+H⁺]. *Anal. Calc.* for C₃₀H₂₇ClO₃Ru₂S₃ (769.32): C, 46.84; H, 3.54. Found: C, 46.92; H, 3.63%.

3.9. [Ru₂(*p*-CH₃–C₆H₄–^{*i*}Pr)₂(S–C₆H₄–*p*-OH)₃]Cl (**4b**)

IR (KBr): $\tilde{\nu}$ = 3438 (OH). ¹H NMR (200 MHz, [*d*₆]DMSO) δ (ppm): 9.85 (3H, s; OH), 7.68 (d, ³*J* = 8.6 Hz, 6H; *H*–*Ar*), 6.80 (d, ³*J* = 8.6 Hz, 6H; *H*–*Ar*), 5.58 (d, ³*J* = 4.9 Hz, 2H; *H*–*Ar*), 5.38 (d, ³*J* = 4.9 Hz, 2H; *H*–*Ar*), 5.26 (d, ³*J* = 4.9 Hz, 2H; *H*–*Ar*), 5.21 (d, ³*J* = 4.9 Hz, 2H; *H*–*Ar*), 1.93 (sept, ³*J* = 6.8 Hz, 2H; (CH₃)₂CH), 1.55 (6H, s; CH₃), 0.85 (d, ³*J* = 6.8 Hz, 6H; (CH₃)₂CH), 0.74 (d, ³*J* = 6.8 Hz, 6H; (CH₃)₂CH). ¹³C NMR (50 MHz, [*d*₆]DMSO) δ (ppm): 21.31 ((CH₃)₂CH), 21.61 ((CH₃)₂CH), 30.71 (CH₃), 70.12 ((CH₃)₂CH), 106.895 (*C*–*Ar*), 115.73 (*C*–*Ar*), 125.20 (*C*–*Ar*), 127.36 (*C*–*Ar*), 134.10 (*C*–*Ar*), 158.1 (*C*(O)). MS (ESI) *m/z*: 847 [*M*+H⁺]. *Anal. Calc.* for C₃₈H₄₃ClO₃Ru₂S₃ (881.54): C, 51.77; H, 4.92. Found: C, 51.86; H, 4.98%.

3.10. $[Ru_2(C_6(CH_3)_6)_2(S-C_6H_4-p-OH)_3]Cl$ (**4c**)

IR (KBr): $\tilde{\nu}$ = 3430 (OH). 1H NMR (200 MHz, CD_3OD) δ (ppm): 7.77 (d, $^3J = 8.0$ Hz, 6H; *H-Ar*), 7.16 (d, $^3J = 8.0$ Hz, 6H; *H-Ar*), 1.71 (36H, s; CH_3). ^{13}C NMR (50 MHz, $[d_6]DMSO$) δ (ppm): 115.9 (*C-Ar*), 125.4 (*C-Ar*), 132.3 (*C-Ar*), 133.6 (*C-Ar*), 144.5 *C(O)*. MS (ESI) m/z : 903 [$M+H^+$]. *Anal. Calc.* for $C_{42}H_{51}ClO_3Ru_2S_3$ (937.64): C, 53.80; H, 5.48. Found: C, 53.12; H, 4.98%.

4. Conclusion

In the present study we showed that dinuclear (arene)ruthenium units react only with the SH function of mercaptoalcohols, thus providing an easy and high-yield route to diruthenium trithiolato complexes containing free OH functions in the thiolato ligands. It should be possible to use these compounds for the build-up of multinuclear complexes or metallodendrimers by functionalisation of the hydroxy groups.

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