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MS-TOF Study of the Formation of Thiolato-Bridged Rhodium Oligomers

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The complex [Cp*Rh(μ-SPh)$_3$RhCp*]Cl was used as a starting material to synthesize various oligomeric materials of the general formula [Cp*Rh(μ-SPh)$_x$(μ-Cl)$_{3-x}${Rh(μ-SPh)$_3$}$_n$-RhCp*] (x = 1 to 3; n = 1 to 4), which are formally formed by insertion of nRh(SPh)$_3$ units into one μ-Rh–SPh bond. The insertion of Ir(SPh)$_3$ was also observed to generate the heterotrimetallic species. All complexes were observed by using HRMS-TOF and [Cp*Rh(μ-SPh)$_3$Rh(μ-SPh)$_3$RhCp*]Cl, [**3**$^+$]Cl, was characterized by using X-ray crystallography.

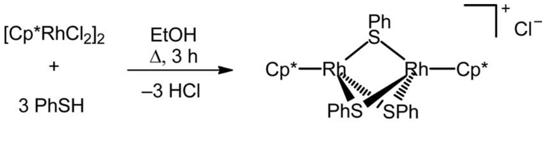
Introduction

Polynuclear thiolato complexes of transition metals have been widely studied for their structural, chemical, and electronic properties,[1] and as models for active centers in biomolecules.[2] Many μ-thiolato-bridged metal oligomers of the general formula [M(μ-SR)$_x$]$_n$ have been reported, where x = 1–4, with a wide variety of metals, oxidation states, and ancillaries.[3] More specifically, the dimeric species [CpRh(μ-p-SC$_6$H$_4$Me)$_3$RhCp]$^+$ (Cp = η^5-C$_5$H$_5$)[4] and [Cp*Rh(μ-SR)$_3$RhCp*]$^+$ (Cp* = η^5-C$_5$Me$_5$) have been reported for Rh^{III} where R = Ph, iBu, allyl,[5] Me,[6] H,[7] or fluorinated aromatics.[8] Further functionalization of the bridging thiolato group for specific purposes was also accomplished by esterification with R = p-C$_6$H$_4$OH[9] or Suzuki coupling with R = p-C$_6$H$_4$Br.[10]

Although the rhodium centers in each of these complexes are 18-electron saturated species, the thiolato ligands can shift from a bridging to a terminal position, giving access to free coordination sites that can become available for incoming ligand coordination. For example, the binding of a substrate can occur in the complex CpMo(μ-SMe)$_3$(μ-Cl)-MoCp by opening of a chlorido bridge by controlled redox chemistry.[11] Of course, other factors, such as pH, can modify the coordination mode of the thiolato ligand.[12] It was therefore expected that under the correct experimental conditions, the addition of n equivalents of [Rh(SPh)$_3$][3a] to triply bridged thiolato binuclear Cp*Rh^{III} complexes would yield new thiolato bridges that would form oligomeric clusters with added n[Rh(SPh)$_3$]. Such stepwise control could eventually lead to the formation of hybrid metal–organic polymers if good control of the insertion process was achieved.[13] To gain more insight on the possibility of such transformations, time-of-flight (TOF) high-resolution mass spectrometry (HRMS) studies were undertaken.[14]

Results and Discussion

The complex [Cp*Rh(μ-SPh)$_3$RhCp*]Cl ([**1**$^+$]Cl) was used as a substrate and was synthesized by adding thiophenol to a refluxing solution of [Cp*RhCl$_2$]$_2$ in technical-grade ethanol, as described by Chérioux and co-workers for the synthesis of [Cp*Rh(μ-p-SC$_6$H$_4$OH)$_3$RhCp*]Cl (Scheme 1).[9] The HRMS spectrum of a solution of [**1**$^+$]Cl in CH$_2$Cl$_2$ shows the single ion [Cp*Rh(μ-SPh)$_3$RhCp*]$^+$ (**1**$^+$) (m/z = 803.08), as expected. The ^{1}H NMR spectrum in [D]chloroform exhibits multiplets in the aromatic region corresponding to the *ortho* hydrogen atoms of the thiophenolato ligands at δ = 7.82–7.77 and to the *meta* and *para* hydrogen atoms at δ = 7.40–7.33, as well as a singlet at δ = 1.34 accounting for the 30 protons of the two Cp* ligands. This is in perfect accordance with the ^{1}H NMR spectroscopic data for complex **1**$^+$, which has previously been characterized as the triflate salt [**1**$^+$]OTf.[5]



1$^+$ (m/z = 803.08)

Scheme 1. Synthesis of dinuclear complex [Cp*Rh(μ-SPh)$_3$RhCp*]-Cl ([**1**$^+$]Cl).

The ethanol solution proves perfectly adequate to obtain [**1**$^+$]Cl cleanly, as only **1**$^+$ was observed (m/z = 803.08, 100%) by HRMS after heating [**1**$^+$]Cl for 48 h at reflux with RhCl$_3$·xH$_2$O (x = 2 or 3) and PhSH (3 equiv.). However, heating a solution [**1**$^+$]Cl at reflux in toluene, where the salt is not totally soluble, and then dissolving the residues in

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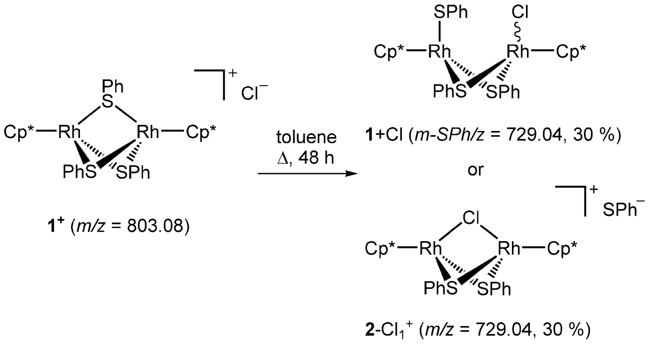
dichloromethane, affords by HRMS species [Cp*Rh(Cl)(μ-SPh)$_2$RhCp*]$^+$ (**2**-Cl$_1$$^+$; *m*/*z* = 729.04, 30 %) in addition to **1**$^+$ (*m*/*z* = 803.08, 70 %; Scheme 2). The low dielectric constant of toluene compared to that of ethanol suggests that the neutral complex [Cp*Rh(Cl)(μ-SPh)$_2$Rh(SPh)Cp*] **1**+Cl is favored in toluene and could show as the [M –SPh] peak in the mass spectrum. Similar neutral binuclear rhodium(III) Cp* complexes are know in which the rhodium centers are bridged by two thiolato ligands and each contains one nonbridging chlorido ligand either in a *syn*[6b] or *anti* conformation.[7] In addition, the cationic binuclear analogue [CpRh(μ-*p*-SC$_6$H$_4$Me)$_2$(μ-Cl)RhCp]$^+$ has been reported with the weakly coordinated SbCl$_6$ counteranion.[4a] It should be noted, however, that if the species observed (*m*/*z* = 729.04) corresponds to a cationic complex, it has to contain a phenylthiolato counteranion. Whereas it is much less likely to observe a phenylthiolato counteranion rather than chlorido or SbCl$_6$, the formation of a cationic analogue of [**1**$^+$]Cl having a bridging chloride ligand and a thiophenolato anion [Cp*Rh(μ-Cl)(μ-SPh)$_2$RhCp*]SPh [**2**-Cl$_1$$^+$]SPh cannot be discarded, as a few transition-metal complexes are known to have such phenylthiolato counterions.[15]



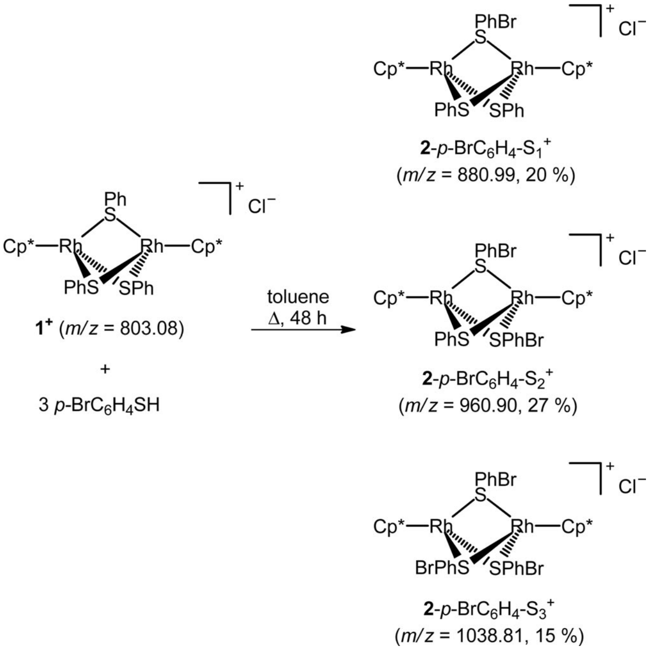
Scheme 2. Formation of neutral complex **1**+Cl or cationic complex **2**-Cl$_1$$^+$.

A similar solvent effect was observed by Maitlis and coworkers, where the position of the equilibrium between the ionic [Cp*Rh(μ-SAr$_f$)$_3$RhCp*][Cp*Rh(SAr$_f$)$_3$] (Ar$_f$ = C$_6$F$_5$) and neutral Cp*Rh(SAr$_f$)$_2$ complexes depended on the polarity of the solvent.[8] The implication of these observations is that in nonpolar solvents, one of the thiolato bridge opens, thus leaving one coordination site available for further bonding interactions with the chloride counteranion or other nucleophiles in its environment. Therefore, it should be possible to observe chain growing of an inorganic precursor through the controlled addition of [Rh(SR)$_3$]$_n$ units.

Ligand Exchange

Polar solvents, such as ethanol, water, and DMF, seem to inhibit any ligand exchange or addition reactions. Indeed, after mercaptans or [Rh(SPh)$_3$]$_n$[3a] are added to a solution of [**1**$^+$]Cl and heated for 48 h under refluxing conditions, only **1**$^+$ was observed when an aliquot of the solution was diluted in CH$_2$Cl$_2$ and analyzed by HRMS (*m*/*z* = 803.08). Therefore, as stated previously, toluene was chosen as the solvent of choice for reactions with [**1**$^+$]Cl. Addition of *t*BuSH (3 equiv.) to [**1**$^+$]Cl in toluene resulted in a very slow exchange of thiol. Only trace amounts of [Cp*Rh(μ-S-*t*Bu)(μ-SPh)$_2$RhCp*]$^+$ (*m*/*z* = 783.11) (**2**-*t*BuS$_1$$^+$) were obtained after 48 h in refluxing toluene.

Under the same reaction conditions, however, an exchange between thiophenolato and *p*-bromothiophenolato ligands occurs to give a mixture of [**1**$^+$]Cl (30 %), [Cp*Rh(μ-S-*p*-BrC$_6$H$_4$)(μ-SPh)$_2$RhCp*]$^+$ (*m*/*z* = 880.99, 20 %; **2**-*p*-BrC$_6$H$_4$-S$_1$$^+$), [Cp*Rh(μ-S-*p*-BrC$_6H_4$)$_2$(μ-SPh)RhCp*]$^+$ (*m*/*z* = 960.90, 27 %; **2**-*p*-BrC$_6$H$_4$-S$_2$$^+$), and [Cp*Rh(μ-S-*p*-Br-C$_6$H$_4$)$_3$RhCp*]$^+$ (*m*/*z* = 1038.81, 15 %; **2**-*p*-BrC$_6$H$_4$-S$_3$$^+$; Scheme 3). The protonation of the phenylthiolato ligand by more acidic *p*-BrC$_6$H$_4$SH and the coordination of the conjugate base of the latter mercaptan is therefore favored, as expected.[12e]



Scheme 3. Ligand exchange of [**1**$^+$]Cl with *p*-BrC$_6$H$_4$SH to form [Cp*Rh(μ-SPh)$_{3-x}$(μ-S-*p*-BrC$_6$H$_4$)$_x$RhCp*]Cl {*x* = 1, [**2**-*p*-BrC$_6$H$_4$-S$_1$$^+$]Cl; *x* = 2, [**2**-*p*-BrC$_6$H$_4$-S$_2$$^+$]Cl; and *x* = 3, [**2**-*p*-BrC$_6$H$_4$-S$_3$$^+$]Cl}.

Formation of Oligomers

After the addition of one equivalent of rhodium(III) chloride and three equivalents of thiophenol to a solution of [Cp*Rh(μ-SPh)$_3$RhCp*]Cl, [**1**$^+$]Cl, in toluene, the reaction mixture was heated under reflux for 48 h. It should be noted that in most of these reactions, an aliquot of the toluene solution was taken and diluted in methylene chloride for HRMS analysis. Unless stated otherwise, the products exhibit poor solubility, and a solid residue is present in the reaction flask, which can account for more than 70 % of the overall yield of material. However, when dissolving the residual solid in dichloromethane, the product distribution observed by HRMS does not differ significantly from the one in the original aliquot of the toluene solution. (See the Supporting Information for HRMS data supporting this statement) NMR spectroscopy proves to be unreliable to get chemical information on this system for two reasons. First, the low solubility of the solids in usual NMR solvents in most of the experiments makes the acquisition of good data and the isolation of each species difficult. Also, the solutions obtained contain complex mixtures of many species that all have very similar signatures to the starting materials. This results in very broad resonances in the ^{1}H NMR spectra and very weak or absent resonances in the ^{13}C{^{1}H} NMR spectra, even with over 8000 acquisitions (^{1}H and ^{13}C{^{1}H} NMR spectra for a typical oligomerization reaction along with the corresponding HRMS spectrum are given in the Supporting Information). The only species that could be identified by ^{1}H NMR spectroscopy is [**3**$^+$]Cl, which has a single resonance for the Cp* region at a chemical shift of δ = 1.27 ppm.

The HRMS spectrum in CH_2Cl_2 of the previously mentioned reaction reveals many new species, among which the anticipated compound [Cp*Rh(μ-SPh)$_3$Rh(μ-SPh)$_3$RhCp*]Cl, [**3**$^+$]Cl, as the cationic ion [Cp*Rh(μ-SPh)$_3$Rh(μ-SPh)$_3$RhCp*]$^+$ (**3**$^+$, *m*/*z* = 1233.02) in a 1% yield only (Table 1, Entry 1). The species containing one or two chlorido ligands, [**3**-Cl$_1$$^+$] (*m*/*z* = 1158.98) and [**3**-Cl$_2$$^+$] (*m*/*z* = 1084.93), were also observed in 12 and 1% yield, respectively, as well as the tetrameric complex with one chlorido ligand, [Cp*Rh(μ-SPh)$_2$ClRh(μ-SPh)$_3$Rh(μ-SPh)$_3$RhCp*]$^+$, [**4**-Cl$_1$$^+$] (*m*/*z* = 1588.92), in 4% yield (Scheme 4). Addition of one more equivalent of $RhCl_3$ and three equivalents of thiophenol to this reaction mixture shifts the equilibrium towards tri-, tetra-, and pentanuclear rhodium species after heating for another 24 h under refluxing conditions (Table 1, Entry 2). This shows the possibility of controlling the distribution of the oligomers by stepwise addition of the reagents. The yields for the tri- and tetranuclear compounds after heating at reflux for 48 h are higher if $RhCl_3$ and PhSH are stirred in methanol under reflux for 2 h and dried to give an orange powder of oligomeric [Rh(SPh)$_3$]$_x$[3a] before adding to the solution of [**1**$^+$]Cl (Table 1, Entry 3). In this last reaction mixture, addition of thiophenol (3 equiv.) does not result in the replacement of the chlorido ligands by thiolato as expected. Instead it shifts the product distribution towards the binuclear species (Table 1, Entry 4).

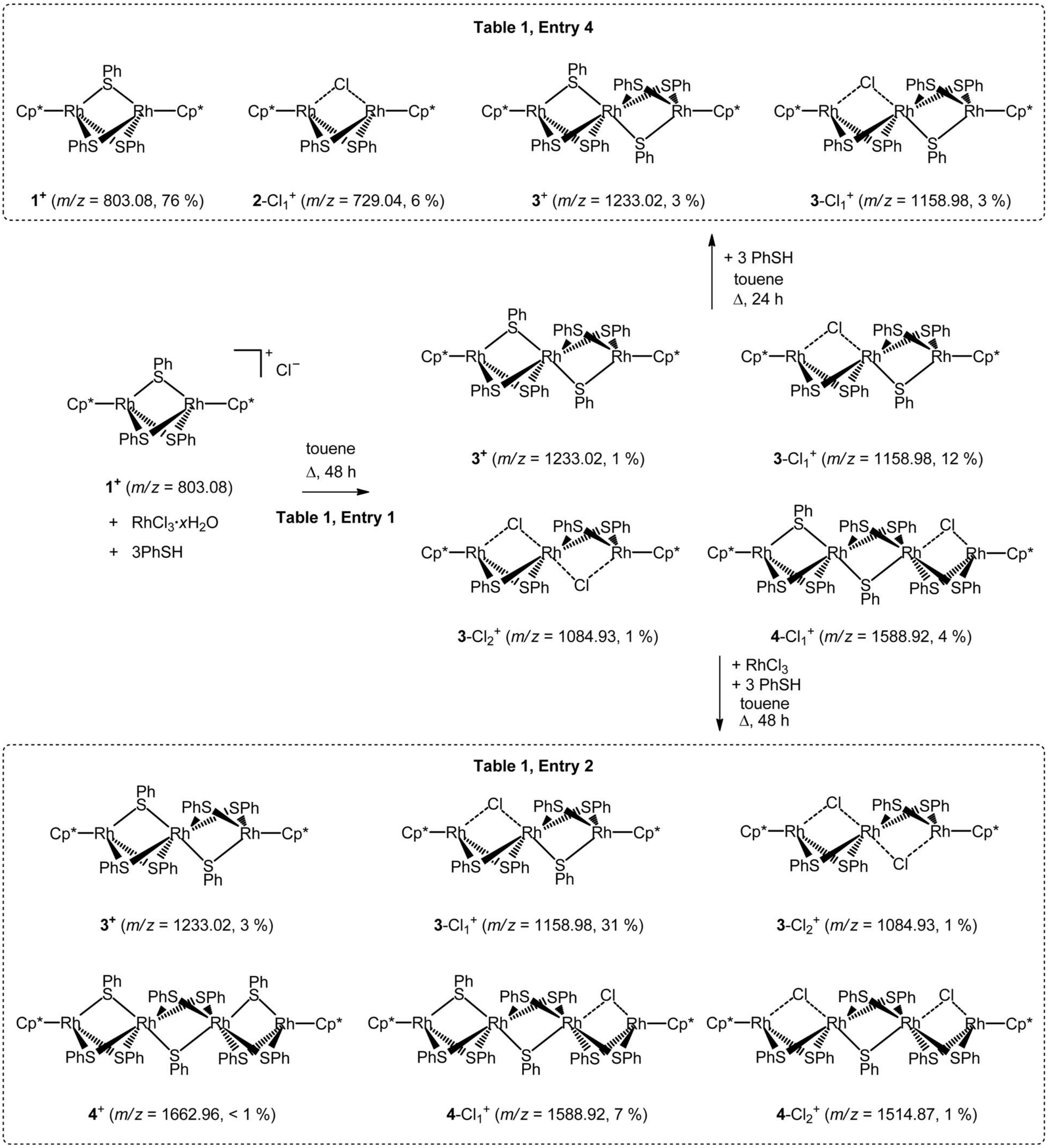
Just like the coordinating solvents inhibit the chain growing process, an excess amount of thiol or coordinating bases, such as NEt_3, also prevent the insertion of RhX_3 (X = Cl or SR) species (Table 1, Entry 5; NEt_3) even after heating at reflux for 12 d (Table 1, Entry 6). The addition of three equivalents of HCl (2% in Et_2O), on the other hand, favors insertion and greatly helps to increase the solubility of the resulting mixture. Indeed, a clean red solution is obtained after 48 h in refluxing toluene. The HRMS spectrum of this solution reveals di-, tri-, and tetrarhodium species, [**2**-Cl$_2$$^+$], [**3**-Cl$_{0,1,2,3}$$^+$], and [**4**-Cl$_{0,1,2,3}$$^+$], most of which were separated by HPLC and identified by HRMS; all errors were under 5 ppm. (See the Supporting Information for HPLC chromatogram and HRMS data) Trace amounts of compounds were also observed, whose *m*/*z* ratios correspond to the penta- and hexanuclear thiolato-bridged rhodium analogues of **3**$^+$ each containing two Cp* ligands, and, respectively, one or two chlorido ligands, [**5**-Cl$_{1,2}$$^+$], and two or three chlorido ligands, [**6**-Cl$_{2,3}$$^+$], (Table 1, Entry 7). Possible structures of these complexes are depicted in Scheme 5, although the exact structures, particularly the position of the chloride ligands, cannot be deducted from the HRMS data. It can be speculated that the acid protonates the thiophenolato ligand, therefore helping to open a coordination site for chloride coordination to form the neutral analogue, which should have better solubility in toluene. Dilution of this reaction mixture in excess ethanol (10× the volume) once again resulted in the displacement of the product distribution towards the dimeric species (Table 1, Entry 8), putting forward the dynamic process at hand. When the reaction was carried out in a biphasic system (toluene/water, 1:1) with NBu_4Br as a phase-transfer agent, a distribution where the thiolate ligands are favored over the chloride ligands was observed (Table 1, Entry 9). Finally, high yields in trinuclear compounds (50%) can be obtained by heating [**1**$^+$]Cl, $RhCl_3$, and thiophenol in xylene under reflux; however, a large amount of decomposition to unidentifiable compounds of mass ranging from 600 to 2000 is obtained (34%) (Table 1, Entry 10).

Table 1. Distribution of oligomers formed by addition of [RhCl$_x$(SPh)$_{3-x}$] units to [**1**$^+$]Cl.

Entry[a]	**1**$^+$ [%]	Rh$_2$[b] [%]	**3**$^+$ [%]	Rh$_3$ [%]	**4**$^+$ [%]	Rh$_4$ [%]	Other[c] [%]
1	35	77	1	14	0	4	5
2	13	37	3	35	<1	8	20
3	3	3	15	76	1	18	3
4	76	82	3	6	0	2	10
5	78	96	0	2	0	0	2
6	44	70	2	17	0	2	11
7	0	19	6	50	1	24	7
8	0	65	1	20	0	4	11
9	74	74	6	6	3	4	16
10	10	10	0	50	0	6	34

[a] See the Supporting Information for complete distribution of products and detailed reaction conditions. [b] Rh$_x$: Content of species containing *x* rhodium atoms, including the parent X$^+$ species. [c] Other species include Rh$_5$ and Rh$_6$ as well as unidentified compounds with *m*/*z* values ranging from 600 to 2000 amu.

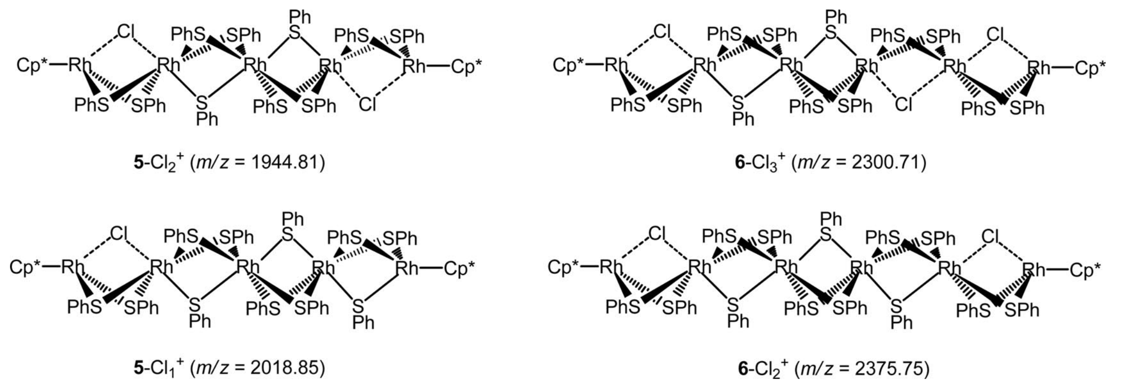
According to the proposed reaction scheme, it could be possible to form heterometallic complexes by using the same strategy. Indeed, the addition of one equivalent of $IrCl_3$ and three equivalents of PhSH to a solution of [**1**$^+$]Cl in toluene with HCl resulted in the insertion of the Ir^{III} fragment to give [Cp*Rh(μ-SPh)$_3$Ir(μ-SPh)$_3$RhCp*]$^+$ [**3Ir**$^+$] (*m*/*z* = 1323.08, <1%) as well as the chloride-containing compound [**3Ir**-Cl$_1$$^+$] (*m*/*z* = 1249.03, 12%), albeit in low yields (Scheme 6). It should be noted, however, that the addition of iron(III) chloride did not yield any insertion product.



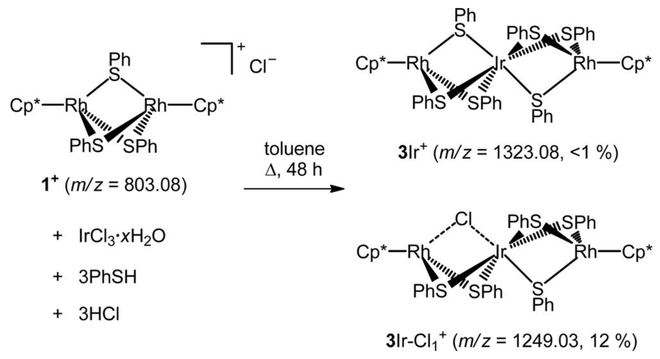
Scheme 4. Formation of oligomers by stepwise insertion of $Rh(SPh)_{3-x}Cl_x$ units into dinuclear cation **1**$^+$. The chlorido-containing species are depicted as cationic species bearing bridging chlorido ligands; however, as previously discussed they may also exist in their neutral form containing an additional chlorido or phenylthiolato ligand, in which case the species observed by HRMS would be [M – Cl] or [M –SPh], respectively.

Structure of [3$^+$]Cl

It was possible to isolate single crystals of complex [**3**$^+$]-Cl, which were analyzed by X-ray crystallography.[16] The ORTEP diagram is shown in Figure 1. The complex crystallizes in the $P2_1/c$ space group with $Z = 4$, but with two independent molecules. For each of the molecules, the central rhodium atoms are located on inversion centers. The trimetallic structure has all Rh atoms aligned (the Rh–Rh–Rh angle is 180°), where the two terminal metal centers have piano-stool conformation and with the central atom adopting a pseudo-octahedral geometry. The Rh–S distances on the terminal rhodium atoms vary from 2.377(3) to 2.420(3) Å, whereas the central rhodium atoms have Rh–S distances that vary from 2.350(3) to 2.385(3) Å. The phenyl rings of bridging thiophenolato ligands are rotated



Scheme 5. Putative structures of the penta- and hexanuclear complexes [**5**-$Cl_{1,2}^+$] and [**6**-$Cl_{2,3}^+$]. The exact position of the chlorido ligands on the chain is unknown as is its bridging or terminal position, as these complexes were identified on the basis of HRMS results.



Scheme 6. Formation of [Cp*Rh(μ-SPh)$_3$Ir(μ-SPh)$_3$RhCp*]$^+$ [**3**Ir$^+$] and [Cp*Rh(μ-SPh)$_2$ClIr(μ-SPh)$_3$RhCp*]$^+$ [**3**Ir-Cl$_1^+$] by insertion of an Ir fragment into [**1**$^+$]Cl.

by an average angle of 29.4° from the plane formed by the three sulfur atoms in *fac* position of the terminal Rh atoms. Interestingly, there is no significant π stacking between the thiophenolato ligands within a molecule.

Two types of disorder were observed in this crystal structure, accounting for the relatively high *R* factor (5.96%). First, on one of the complexes, the Cp* ring has rotational disorder. Additionally, it was possible to observe in the Fourier map the presence of large Q peaks in proximity to the rhodium centers that were attributed to the sulfur atoms. The refinement of the occupation for the two independent molecules gave ratios of 85:15 and 90:10 between the sulfur atoms of the thiophenolato ligands that were originally assigned and the residual Q peaks. Although no new phenyl ring was assigned to the minor sulfur components, the orientation of the phenyl ring suggests that in some of the molecules, the thiophenolato ligands adopt a counterclockwise orientation relative to the major component (Figure 2). Therefore, no good model for the phenyl rings of the minor components was found to withstand the structure refinements.

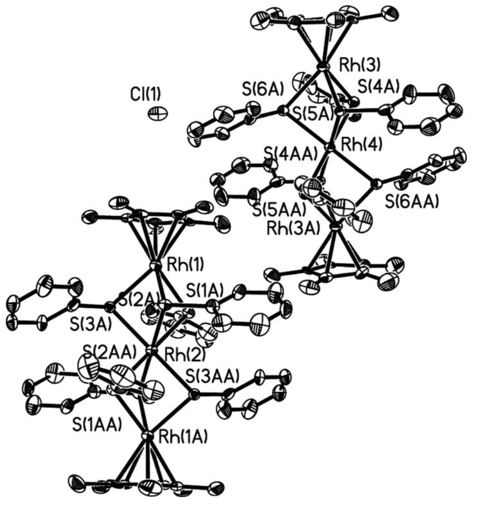


Figure 1. ORTEP view of [**3**$^+$]Cl showing the numbering scheme adopted. Anisotropic atomic displacement ellipsoids for the non-hydrogen atoms are shown at the 50% probability level. Hydrogen atoms were removed for clarity. The symmetry transformation used to generate equivalent atoms is –*x*, –*y*, –*z*.

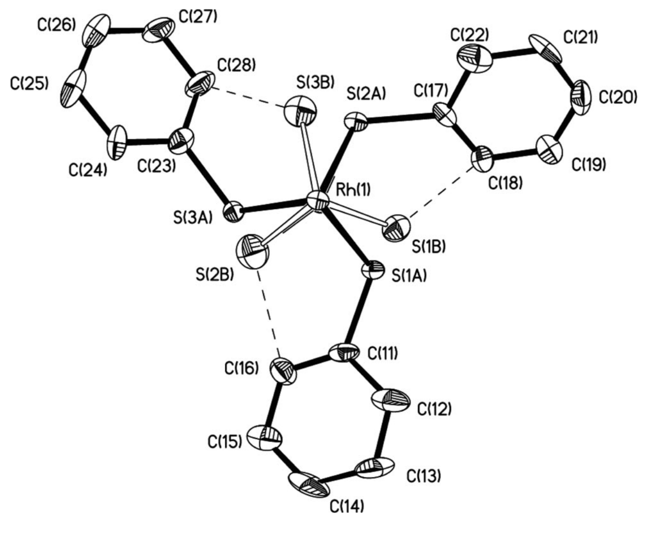


Figure 2. ORTEP view of one of the Rh(SPh)$_3$ fragments of [**3**$^+$]Cl in the *fac* conformation. The Q peaks that were labeled as sulfur atoms show possible disorder where the thiophenolate ligands are in a counterclockwise orientation compared to the original model.

Conclusions

The complex [Cp*Rh(μ-SPh)$_3$RhCp*]Cl shows a propensity to open up a coordination site in nonpolar solvents and under acidic conditions to favor the insertion of nRh(SPh$_3$)$_3$ units to form [Cp*[Rh(μ-SPh)$_3$]$_n$RhCp*]Cl and its chlorido derivatives. The oligomeric material formed, which consists of species having up to six rhodium atoms, were observed by using HRMS-TOF. Although the isolation and the purification of these complex mixtures prove to be quite difficult on the scale that the reactions were carried out on, it is nevertheless possible to use HPLC to observe them individually. The crystal structure of [**3**$^+$]Cl confirms a linear trimeric species. Although similar coordination environments could be obtained with species having more than three metal atoms, no structural proof could be obtained that a similar arrangement is present in higher rhodium-containing clusters. Current studies are aimed at the isolation of larger species to confirm their solid-state structures and at increasing the selectivity in the distribution of the products.

Experimental Section

The complex [Cp*Rh(μ-SPh)$_3$RhCp*]Cl, [**1**$^+$]Cl, was prepared according to a literature procedure for [Cp*Rh(μ-*p*-SC$_6$H$_4$OH)$_3$-RhCp*]Cl.[9] The HRMS analyses were performed with an Agilent 6210 Time-of-flight LC–MS with an electrospray ion source. Samples for HRMS analysis were prepared by taking a 10-μL aliquot of the desired solution and diluting it in dichloromethane (1 mL), or by dissolving a few milligrams of solid material in dichloromethane (1 mL), after which the solutions were filtered (0.2 μm) for direct injection. ^{1}H NMR spectra were recorded with a Varian Inova NMR AS400 spectrometer at 400.0 MHz.

For the ligand exchange reactions, the thiol (3 equiv.) was added to [**1**$^+$]Cl (10 mg, 0.012 mmol) in a round-bottomed flask in the appropriate solvent (10 mL), after which the solution was heated to reflux, and the samples were taken for HRMS analysis at 24-h intervals.

For the formation of the oligomers (Table 1), unless stated otherwise, RhCl$_3$·xH$_2$O (3.0 mg, 0.012 mmol) and HSPh (3.6 μL, 0.036 mmol) were added to [**1**$^+$]Cl (10 mg, 0.012 mmol) in toluene (10 mL) in a round-bottomed flask, and the mixture was heated at 110 °C for 48 h. An aliquot of the solution was dissolved in CH$_2$Cl$_2$ for HRMS analysis. The percentage given represents the HRMS intensity of one fragment compared to the summation of the intensity for all fragments observed. In some of the entries, the solvent was removed under reduced pressure and extracted with CH$_2$Cl$_2$. An aliquot was taken to confirm that the species observed in the toluene solution was the same as that in the bulk sample (Supporting Information). ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded for some of the samples, but yielded very little information other than the identification of [**1**$^+$], which has been previously characterized as the triflate salt,[5] and [**3**$^+$]Cl, which has a ^{1}H NMR chemical shift for the Cp* ring of 1.27 ppm. Typical NMR spectra are shown in the Supporting Information.

Supporting Information (see footnote on the first page of this article): Reaction conditions, product distributions and corresponding mass spectra for the ligand exchange and oligomer formation reactions; results of HPLC separation of the complexes and their characterization with relative errors; crystallographic details for [**3**$^+$]Cl.

Acknowledgments

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