## Substituent dependence of the reactions of [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] with bulky aromatic thiols<sup>†</sup>‡

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2,4,6-Trialkylbenzenethiols react with [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] to give Ru products with the alkyl substituents forming M–C  $\sigma$  bonds, carbene, carbene with a S  $\alpha$ -heteroatom, agostic hydrogen interaction or a simple tetrahedral Ru(II) species, depending on the substituent.

<sup>†</sup> Complex 1: [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] (0.60 g; 0.63 mmol) was dissolved in degassed acetone, Htmt (0.29 g; 1.90 mmol) and triethylamine (0.39 g; 3.86 mmol) were added. The solution was heated under reflux, MeOH (20 mL) added and the solution left to give X-ray quality crystals from the reaction solution. Yield: 0.18 g, 35%. Elemental analysis for C<sub>45</sub>H<sub>47</sub>PRuS<sub>3</sub> calcd: C 66.2, H 5.8, found: C 66.2, H 5.9%. Selected data: <sup>1</sup>H NMR (300 MHz, (acetone-d<sub>6</sub>) δ 7.79-7.73 (m, 6H, PPh<sub>3</sub>), 7.53-7.50 (m, 9H, PPh<sub>3</sub>), 6.88 (s, Ph, 2H), 6.60, (s, Ph, 1H), 6.54, (s, Ph, 2H), 6.02, (s, Ph, 1H), 2.43 (d, 2H  ${}^{3}J_{\rm PH} = 6.6\,{\rm Hz}, CH_{2}$ , 2.30 (s, 3H, CH<sub>3</sub>), 2.25 (s, 6H, CH<sub>3</sub>), 2.15 (s, 6H, CH<sub>3</sub>), 2.02 (s, 3H, CH<sub>3</sub>), 1.40 (s, 6H, CH<sub>3</sub>), <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  27.3 (s, Ru–*PP*h<sub>3</sub>), <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  30.8 (*C*H<sub>2</sub>), 22.0 (CH<sub>3</sub>), 20.9 (CH<sub>3</sub>), 20.6 (CH<sub>3</sub>), 20.5 (CH<sub>3</sub>), 19.3 (CH<sub>3</sub>). Complex 2: [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] (0.60 g; 0.63 mmol) was dissolved in degassed MeOH and 2 equiv. of Htmt was added and a two fold excess of triethylamine. The solution was stirred at room temperature. The solution was filtered to give the complex and washed with MeOH. Yield: 0.35 g, 57%. Elemental analysis for C<sub>54</sub>H<sub>50</sub>P<sub>2</sub>RuS<sub>2</sub>·C<sub>3</sub>H<sub>6</sub>O calcd: C 69.6, H 5.7; found: C 68.7, H 5.9%. Selected data: <sup>1</sup>H NMR (300 MHz,  $CD_2Cl_2$ )  $\delta$  14.15 (t, 1H <sup>3</sup> $J_{PH}$  = 7.5 Hz, CH), 7.12–6.97 (m, 30H, PPh<sub>3</sub>), 6.60 (s, Ph, 2H), 6.07 (s, Ph, 1H), 6.06 (s, Ph, 1H), 2.18, (s, 3H, CH<sub>3</sub>), 2.17, (s, 3H, CH<sub>3</sub>), 2.08 (s, 6H, CH<sub>3</sub>), 1.72 (s, 3H, CH<sub>3</sub>);<sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CDCl<sub>3</sub>): δ 29.5, (s, Ru–PPh<sub>3</sub>) 46.4, (s, Ru–*P*Ph<sub>3</sub>), <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): δ 160.5 (Ru=*C*H), 22.5 (CH<sub>3</sub>), 20.9 (CH<sub>3</sub>), 20.3 (CH<sub>3</sub>), 20.0 (CH<sub>3</sub>). Complex 3: Synthesized from equilibrium of 1 and 2. The solution was left to give complex 3 as a crop of X-ray quality crystals following the addition of cyclohexane. Yield: approx. 20%. Elemental analysis for C<sub>63</sub>H<sub>60</sub>P<sub>2</sub>RuS<sub>3</sub> calcd: C 70.5, H 5.7; found: C 70.2, H 6.7%. Selected data: <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 2.47 (s, 3H, CH<sub>3</sub>), 2.41 (s, 3H, CH<sub>3</sub>), 2.25 (s, 3H, CH<sub>3</sub>), 2.23 (s, 3H, CH<sub>3</sub>), 1.83 (s,  $3H, CH_3$ , 1.78 (s,  $3H, CH_3$ ), 1.69 (s,  $3H, CH_3$ ), 1.59 (s,  $3H, CH_3$ );  ${}^{31}P{}^{1}H{}$ NMR (121 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  47.8 (d, <sup>2</sup>J<sub>PP</sub> = 15.8 Hz, Ru–PPh<sub>3</sub>)  $\delta$  31.8 (d,  ${}^{2}J_{PP} = 15.8$  Hz, Ru–PPh<sub>3</sub>);  ${}^{13}C{}^{1}H{}$  NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  164.5 (Ru=C). Complex 4:  $[RuCl_2(PPh_3)_3]$  (0.60 g; 0.63 mmol) was dissolved in degassed methanol, Htet (0.37 g; 1.90 mmol) and triethylamine (0.39 g; 3.86 mmol) were added. The solution was stirred for 2 h, filtered and the filtrate left to give X-ray quality crystals from the reaction solution. Elemental analysis for C<sub>54</sub>H<sub>66</sub>P<sub>1</sub>RuS<sub>3</sub> calcd: C 68.8, H 7.1; found: C 69.3, H 7.4%. ES-MS  $m/z = 943.3085 (M^+)$ . Calc mass for  $(C_{54}H_{66}P_1RuS_3) m/z =$ 943.3108. Complex 5: Htipt (0.30 g; 1.27 mmol) and triethylamine (0.25 g; 2.47 mmol) were added to [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] (0.60 g; 0.63 mmol) in acetone (30 mL) and stirred at room temperature for 30 min. The brown solution rapidly changed to green and the complex crystallised out as dark green crystals on standing at 3 °C. Elemental analysis for C<sub>66</sub>H<sub>76</sub>P<sub>2</sub>RuS<sub>2</sub>·C<sub>6</sub>H<sub>12</sub>O<sub>2</sub> calcd: C 71.3, H 7.3; found: C 70.3, H 6.5%.

‡ *Crystal data*: 1: C<sub>45</sub>H<sub>47</sub>PRuS<sub>3</sub>, black plate crystals, M = 816.11, triclinic; space group  $P\bar{1}$ , a = 12.1363(2), b = 16.9452(2), c = 20.2967(2) Å,  $a = 84.3205(4)^\circ$ ,  $\beta = 75.0315(5)^\circ$ ,  $\gamma = 89.0985(5)^\circ$ , V = 4012.42(9) Å<sup>3</sup>, Z = 4, Sterically hindered thiolates have been studied extensively owing to their ability to generate metal complexes with unusual geometries.<sup>1</sup> Such complexes are potentially capable of binding small molecules, but this ability is a sensitive function of the nature of the substituents on the thiolate ligand. We have previously reported the synthesis of complexes of the type  $[Re(SAr)_3(N_2)(PPh_3)]$  $(Ar = 2,4,6-Pr_{3}^{i}C_{6}H_{2})$ <sup>2</sup> We now report our attempted syntheses of analogous Ru systems by the reaction of [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] with aromatic thiolates. Previously complexes of the type  $[Ru(SAr)_4]$ ,  $[Ru(SAr)_4(L)]$  and  $[Ru(SAr)_4(NO)]^-$  (L = MeOH, DMSO, Bu'CN, MeCN or CO,  $Ar = 2,3,5,6-Me_4C_6H_2$  or 2,4,6- $Pr_{3}^{i}C_{6}H_{2}$ , [Et<sub>4</sub>N][Ru(SAr)<sub>3</sub>(C=CPh)Cl] (Ar = 2,6-Me\_{2}C\_{6}H\_{3}),<sup>4</sup>  $[Ru(arene)(SAr)_2]$  (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> or 2,4,6-Pr<sup>i</sup><sub>3</sub>C<sub>6</sub>H<sub>2</sub>),<sup>5</sup> and [Cp\*Ru(Sdmp)] (Sdmp = 2,6-dimesitylthiophenol, Cp\* =  $\eta^{5}$ -C<sub>5</sub>Me<sub>5</sub>)<sup>6</sup> have been described. However, reports of Ru(II) complexes of bulky thiolates with tertiary phosphine co-ligands have been restricted to  $[Ru(SAr)_2(PPh_3)]$  (Ar = 2,6-Ph<sub>2</sub>C<sub>6</sub>H<sub>3</sub>).<sup>7</sup>

Reaction of  $[RuCl_2(PPh_3)_3]$  with 3 equiv. of Htmt (Htmt = 2,4,6-trimethylthiophenol) and triethylamine in dry acetone under dinitrogen gave a dark coloured solution. Following partial evaporation of the solvent, the addition of MeOH gave very dark, almost black crystals of  $[Ru(SC_6H_2Me_2CH_2)(tmt)_2(PPh_3)]$  (1) after standing at room temperature. The isolated yield of crystalline product was 35%. Spectroscopic data for 1 are consistent with

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T = 150 K.  $\mu$ (Mo-K $\alpha$ ) = 0.617 mm<sup>-1</sup>, 66 921 reflections measured, 18 115 unique, 13 264 reflections with  $I > 3\sigma(I)$  used in refinement ( $R_{int} = 0.057$ ). Final R = 0.0498, wR = 0.0579, GoF = 1.0422. **2**: C<sub>57</sub>H<sub>56</sub>OP<sub>2</sub>RuS<sub>2</sub>, Darkbrown fragment, M = 984.22, triclinic; space group  $P\overline{1}$ , a = 11.6056(2),  $b = 13.4790(2), c = 16.3892(3), \text{ Å}, a = 80.9584(8)^{\circ}, \beta = 75.9086(8)^{\circ},$ = 81.6204(8)°, V = 2440.24(7) Å<sup>3</sup>, Z = 2, T = 150 K.  $\mu$ (Mo-K $\alpha$ ) = 0.512 mm<sup>-1</sup>, 42120 reflections measured, 11062 unique, 6861 reflections with  $I > 3\sigma(I)$  used in refinement ( $R_{int} = 0.067$ ). Final R = 0.0354, wR =0.0384, GoF = 1.1137. **3**: C<sub>75</sub>H<sub>84</sub>P<sub>2</sub>RuS<sub>3</sub>, dark brown crystals, M = 1244.71, triclinic; space group  $P\overline{1}$ , a = 10.9358(2), b = 13.5984(2), c = 23.3454(4) Å,  $a = 100.0944(6)^{\circ}, \beta = 103.0326(6)^{\circ}, \gamma = 103.5247(6)^{\circ}, V = 3191.77(9) \text{ Å}^3,$ Z = 2, T = 150 K.  $\mu$ (Mo-K $\alpha$ ) = 0.437 mm<sup>-1</sup>, 47 600 reflections measured, 14495 unique, 8061 reflections with  $I > 3\sigma(I)$  used in refinement ( $R_{int} =$ 0.069). Final R = 0.0489, wR = 0.0567, GoF = 1.1180. 4: C<sub>54</sub>H<sub>66</sub>PRuS<sub>3</sub>, dark brown block crystals, M = 943.36, triclinic; space group  $P\overline{1}$ , a =12.2271(2), b = 12.4745(2), c = 18.4853(2) Å,  $a = 94.6820(6)^{\circ}$ ,  $\beta = 106.8104(6)^{\circ}$ ,  $\gamma = 110.8996(6)^{\circ}$ , V = 2467.02(6) Å<sup>3</sup>, Z = 2, T = 150 K.  $\mu$ (Mo-K $\alpha$ ) = 0.511 mm<sup>-1</sup>, 33 343 reflections measured, 11 158 unique, 9578 reflections with  $I > 3\sigma(I)$  used in refinement ( $R_{int} = 0.025$ ). Final R = 0.0286, wR = 0.0315, GoF = 1.1121. 5:  $C_{72}H_{88}O_2P_2RuS_2$ , dark green block crystals, M = 1212.64, triclinic; space group  $P\overline{1}$ , a = 12.1170(2), b = 13.7658(2), c = 20.7248(3) Å,  $a = 106.9647(6)^{\circ}, \beta = 91.7024(6)^{\circ}, \beta$  $\gamma = 98.7577(6)^{\circ}, V = 3257.86(9) \text{ Å}^3, Z = 2, T = 150 \text{ K}. \mu(\text{Mo-K}\alpha) =$ 0.397 mm<sup>-1</sup>, 41 524 reflections measured, 14 748 unique, 10 682 reflections with  $I > 3\sigma(I)$  used in refinement ( $R_{int} = 0.043$ ). Final R = 0.0364, wR =0.0405, GoF = 1.0985. CCDC reference numbers 257071–257073, 287812 and 287813. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b515244e

the presence of the cyclometallated thiolate ligand, the  $\sigma$ -bonded carbon C7 appearing at  $\delta$  30.8 ppm in the <sup>13</sup>C NMR. The <sup>1</sup>H NMR spectrum shows three resonances each 6H corresponding to the methyl groups of the two unmetallated ligands. This is due to restricted rotation about the C–S bond which results in the two *o*-Me groups of each thiolate being chemically inequivalent from each other. The <sup>31</sup>P NMR shows as a singlet at  $\delta$  27.3 ppm due to the single phosphorus.

The geometry of the Ru metal centre in 1 is distorted trigonal bipyramidal with the C and P atoms occupying the axial sites. The three thiolate arene groups are directed away from the bulky phosphine ligand to give a cup-like shape to the molecule reminiscent of that found in  $[\text{Re}(\text{tipt})_3(\text{N}_2)(\text{PPh}_3)]^2$  and  $[\text{Mo-(tipt})_3(\text{CO})_2]$  (tipt = 2,4,6-triisopropylthiolate).<sup>1a</sup> Metallation of *o*-Me groups of aromatic thiolates is well known and has been reported to occur for the complex  $[\text{Ru}(\text{SC}_6\text{H-2},3,5,6\text{-Me}_4)_4(\text{NO})]^-$  on standing in methanol.<sup>3</sup>

When reaction 1 was repeated with 2 equiv. of thiol, a new complex  $[Ru(SC_6H_2Me_2CH)(tmt)(PPh_3)_2]$  (2) was isolated as X-ray quality crystals in 57% yield. An ORTEP representation of the structure of complex 2 appears in Fig. 1, together with selected bond lengths and angles. The geometry about the Ru





**Fig. 1** ORTEP diagrams of complexes **2** (top) and **3** (bottom). Selected bond lengths for **2** (Å): Ru(1)-C(7) 1.891(3), Ru(1)-S(1) 2.4143(8), S(1)-C(1) 1.730(3), C(1)-C(6) 1.407(4), C(6)-C(7) 1.433(4). Only the *ipso* carbons of PPh<sub>3</sub> are shown for clarity.

is again approximately trigonal bipyramidal with a PPh<sub>3</sub> group and thiolate sulfur now in the apical sites. The presence of the carbene ligand is shown by the contraction of the Ru–C7 distance from 2.343(6) Å in 1 to 1.891(3) Å in 2. The air stable complex  $[Ru(=CHPh)(N(PPh_2S)_2)_2]$  has a Ru–C distance of 1.88(2) Å, typical for Schrock-type carbenes.<sup>8</sup>



The identity of the product as a carbene complex is confirmed by <sup>1</sup>H NMR which shows a low-field triplet of intensity 1H at  $\delta$ 14.15 ppm assigned to the *CH*=Ru proton ( ${}^{3}J_{HP} = 7.5$  Hz). In the <sup>13</sup>C NMR the low field carbene resonance appears at 160.5 ppm. The <sup>31</sup>P NMR shows a singlet at  $\delta$  29.5 ppm and a broad peak at 46.4 ppm. The broad nature of the second signal combined with lack of P–P coupling suggests that one of the phosphine ligands is dissociating in solution. The *o*-Me carbons in the <sup>13</sup>C NMR are equivalent on the unmetallated thiolate at  $\delta$  22.5 ppm, the remaining methyl resonances appear at 20.9, 20.3 and 20.0 ppm.

The <sup>31</sup>P NMR spectrum of the reaction mixture in acetone with different thiolate ratios shows that both complexes 1 and 2 are present. The ratios are dependent on stoichiometry; with 2 equiv. of thiol they are  $80\% 1 \ 20\% 2$  and with 3 equiv. of thiol  $80\% 2 \ 20\% 1$ . There are two other unidentified Ru(II) species present in solution in small amounts in each case. Also if pure complex 1 is dissolved in acetone and PPh<sub>3</sub> is added there is a slow conversion to complex 2. Conversely when pure 2 is treated with excess thiol in acetone solution it is slowly converted to complex 1. The two species are in equilibrium in the reaction mixtures and are separated by virtue of their differing solubilities, complex 1 being more soluble than 2.

Over a 24 h period at room temperature in  $CD_2Cl_2$  solution the equilibrium mixture of 1 and 2 slowly converts (about 10% as judged by NMR) to a third species [Ru(SC<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>CSC<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>)-(tmt)(PPh<sub>3</sub>)<sub>2</sub>] (3), and the process can be followed by <sup>31</sup>P NMR in  $CD_2Cl_2$ .



Scheme 2 Interconversion of complexes.

The overall geometry about the Ru in complex 3 is again distorted trigonal bipyramidal with one triphenylphosphine and a thiolate sulfur in the apical sites. The Ru–S and Ru–P distances are close to the values found for complex 1. The most striking feature of the structure is the presence of the new carbene ligand with a thiolate group replacing the hydrogen on the carbene carbon of complex 2. Fig. 2 summarises and compares the bond distances within the chelated methyl and carbene ligands for complexes 1 and 3. The formation of the metal carbene bond is apparent from the substantial contraction in the Ru–C distance in moving



Fig. 2 Selected bond lengths (Å) of complexes 1 (left) and 3 (right).

from complex **1** to **2** and **3**. All three structures show evidence for shortening of the C6–C7 bond from the arene ring to the Ru-bound carbon and asymmetry in the C–C distances within the ring, this being most pronounced for **3**. There is, however, no evidence from the bond distances for any olefinic interaction of the arene-CH<sub>n</sub> groups with the metal as observed in complexes such as  $[Ru(1,2-{(CH_2)_2C_6H_4)}(PMe_2Ph)_3].<sup>9</sup>$ 

The mechanism of formation of complexes 2 and 3 is not known at this point. By analogy with the formation of a carbene ligand from a methyl group on iridium<sup>10</sup> it possible that formation of 2 from 1 occurs with hydrogen evolution. However, interfering peaks prevented the observation of the characteristic peak for H<sub>2</sub> in solution by <sup>1</sup>H NMR and no hydrogen evolution was detected by gas-chromatographic analysis. We cannot rule out proton abstraction from the cation formed from 1 on addition of phosphine and loss of thiolate anion. We are currently investigating the details of the mechanism of conversion of 1 to 2.

Chelated carbene complexes with a sulfur co-donor are uncommon and a rare example is the nickel complex with an imidazoylcarbene ligand bearing two  $2-C_6H_4S$  substituents at the 1 and 3 positions. This carbene ligand is, however, not obtained by C–H activation but indirectly from  $CS_2$ .<sup>11</sup>

Ruthenium carbene complexes are of course extremely well known and the complexes described here have some analogy to the second generation Hoveyda–Grubbs catalysts<sup>12</sup> of the type [RuCl<sub>2</sub>(=CH-o-OPr<sup>*i*</sup>C<sub>6</sub>H<sub>4</sub>)(4,5-dihydroIMES)] (IMES = 1,3bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) with the obvious difference that here the thiolate sulfur is almost certainly more strongly bound than the 2-alkoxy substituent. There is no reactivity of these thiolate carbene complexes with olefins and other small molecules.

The reaction of  $[RuCl_2(PPh_3)_3]$  with 3 equiv. of Htet (Htet = 2,4,6-triethylthiophenol) in acetone in the presence of triethylamine also did not give the expected complex of the type [RuL(SAr<sub>3</sub>)(PPh<sub>3</sub>)]<sup>-</sup> core isoelectronic with the known Re complex, but the formally Ru(III) species [Ru(tet)<sub>3</sub>(PPh<sub>3</sub>)] (4). Presumably the anionic Ru(II) species is oxidized during the reaction. Cyclic voltammetry of 4 recorded in DMF confirms a reversible one-electron reduction at  $E_{\frac{1}{2}} = -928$  mV vs. NHE and no oxidation was observed. The EPR measured on 4 in the solid state gave a rhombic set of g-values 2.096, 2.044 and 2.014. These EPR g-values are similar to the Ru(III) complex  $[Ru(dppbt)_3]$  (dppbt = 2-diphenylphosphinobenzenethiolate) that can be oxidized in acetonitrile to form the observable metal-coordinated Ru(III)-thiyl radical complex.<sup>13</sup> The reported g-values for coordinated thivls with Co, Ga and Fe<sup>14</sup> are less anisotropic than 4, but coordination to a 2nd row metal such as Ru is likely to increase anisotropy. However, the similarity to the values reported for [Ru(dppbt)<sub>3</sub>] suggests that this is a Ru(III) complex rather than containing a thiyl radical.

The X-ray crystal structure of **4** reveals that a methylene hydrogen of an ethyl group approaches closely to the Ru and H(2) is within the range normally found for metal–hydrogen agostic interactions. As a result of the formation of this chelate ring the Ru–S(l) bond lies in approximately the same plane as that of the thiolate aryl group, while the remaining Ru–S bonds adopt the more usual conformation perpendicular to the corresponding phenyl rings. The same geometry is seen in [Re(dmt)<sub>3</sub>(PPh<sub>3</sub>)]] (dmt = 2,6-dimethylthiolate),<sup>2</sup> where it is clear that a hydrogen





Fig. 3 ORTEP diagrams of complex 1 (top), 4 (centre) and 5 (bottom). Diagram of complex 1 is one of two crystallographically distinct structures. Only the major orientation of the disordered ethyl or isopropyl groups is shown for 4 and 5, respectively. Only the *ipso* carbons of PPh<sub>3</sub> are shown for clarity.

of the one of the methyl substituents approaches closely to Re (Re–H 2.07 Å), as an agostic interaction.

When the reaction of  $[RuCl_2(PPh_3)_3]$  is carried out with three equivalents of Htipt in acetone a further new complex  $[Ru(tipt)_2(PPh_3)_2]$  (5) can be isolated after partial evaporation of the solvent. There is no evidence for formation of a complex with the Ru(SAr)\_3(PPh\_3) structural motif, presumably due to the increased size of the isopropyl substituents. The crystals of 5 exhibit pronounced pleichroism, appearing dark green or reddishbrown depending on orientation. The overall geometry about the Ru(II) is distorted tetrahedral with no evidence of any interaction between the Ru atom and adjacent H atoms. The interplanar angle between the groups P–Ru–P and S–Ru–S is 66.7°. The shortest Ru  $\cdots$  H distances are 2.93 Å (to H(501)) and 3.04 Å (to H(321)).

The reactions with Ru(II) of alkyl substituted arylthiolates show a strong dependence on the alkyl substituent. 2,4,6-Trimethylbenzenethiol reacts with [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] to give a Ru(Iv) complex with a Ru–C bond to a 2-methylene group which is in a reversible equilibrium with a carbene complex. In solution this reacts further to give a complex of a carbene with a S  $\alpha$ -heteroatom derived from the S–C coupling of two aromatic thiolate ligands. The corresponding thiols with ethyl and isopropyl groups give a paramagnetic Ru(III) complex and a tetrahedral Ru(II) complex respectively, neither of which have Ru–C bonds.

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