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Thermal decomposition of $(C_6Me_6)Ru(\eta^4\text{-}C_4Me_4S)$ and related reactivity and structural studies *

Shifang Luo and Thomas B. Rauchfuss

School of Chemical Sciences, University of Illinois, Urbana, IL 61801 (USA)

Arnold L. Rheingold

Department of Chemistry, University of Delaware, Newark, DE 19711 (USA)

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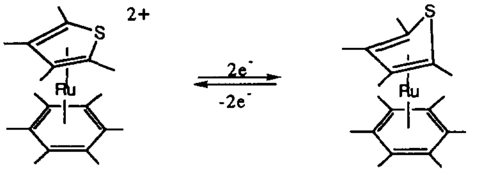
Abstract

The paper focuses on selected aspects of the chemical behavior of $(C_6Me_6)Ru(\eta^4\text{-}C_4Me_4S)$ (**1**). Thermal decomposition of **1** in saturated hydrocarbon solutions yields the trinuclear product $(C_6Me_6)_3Ru_3(C_4Me_4S)_2$ (**2a**) which has been further characterized by single crystal X-ray diffraction. The molecule is centrosymmetric with two $(C_6Me_6)Ru(C_4Me_4S)$ entities coordinated through their sulfur atoms to a central $(C_6Me_6)Ru$ unit. When the thermolysis is conducted in aromatic solvents, we also observed products resulting from arene exchange such as $(arene)(C_6Me_6)_2Ru_3(C_4Me_4S)_2$, where arene = C_6D_6 (**2b**), toluene (**2c**). The $(C_6Me_6)_3$ and arene-exchange products are formed competitively, not consecutively. Compound **2a** is protonated by NH_4PF_6 to give the hydride $[(C_6Me_6)_3Ru_3(C_4Me_4S)_2H][PF_6]$ ([**2a**H]PF_6). Compound **2a**H^+ is structurally dynamic in solution resulting from restricted rotation about the Ru–S axis. Compound **1** decomposes in the presence of H_2 to give the dinuclear dihydride $(C_6Me_6)_2Ru_2(C_4Me_4S)H_2$ (**3**), assigned an unsymmetrical structure where one $(C_6Me_6)Ru$ center is bound to two hydrides and a sulfur atom, while the second $(C_6Me_6)Ru$ is coordinated in an η^4-mode to the thiophene.

Key words: Ruthenium; Thiophene; Sulfur; Desulfurization; Arene; Sandwich complex

1. Introduction

The study of transition metal thiophene complexes in solution [1] represents a historically important and a scientifically fruitful approach to understanding fossil fuel desulfurization pathways [2]. For example, early studies using iron carbonyls provided examples of the homogeneous hydrodesulfurization of benzothiophene [3]. More recent research has focused on the reactivity of preformed thiophene complexes [1,4–8]. In the course of one such study, we described the mixed sandwich compound $(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}C_4Me_4S)$ (**1**) (eqn. (1)). The reactivity of this unique example of a stable Ru^0 thiophene complex arises from its basicity in both the Bronsted and Lewis senses [9]. The present report summarizes studies on other types of reactivity, especially thermal decomposition of **1**.



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(1)

We have previously reported on solution thermolysis of metal thiophene ensembles [3]. This experimental approach provides information comparable to the temperature programmed desorption (TPD) technique which is widely applied in the study the reactivity of chemisorbed substrates [10–12]. Compared with the surface techniques, the solution thermal decomposition approach has the advantage of allowing one to probe

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Correspondence to: Professor T.B. Rauchfuss or Professor A.L. Rheingold.

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the reactivity of the metal–thiophene ensemble with external reagents, an approach incompatible with TPD studies because of the ultra-high vacuum requirements. A second advantage of the solution thermolysis approach is that product characterization is highly reliable.

Ru-thiophene complexes are of interest because of the high activity of Ru-based catalysts in the HDS process [2,12,13]. An additional incentive for this work was the prospect of preparing a triple decker sandwich complex with an $\eta^5:\eta^5$-thiophene ligand, an unknown bonding mode for thiophene [4].

2. Results

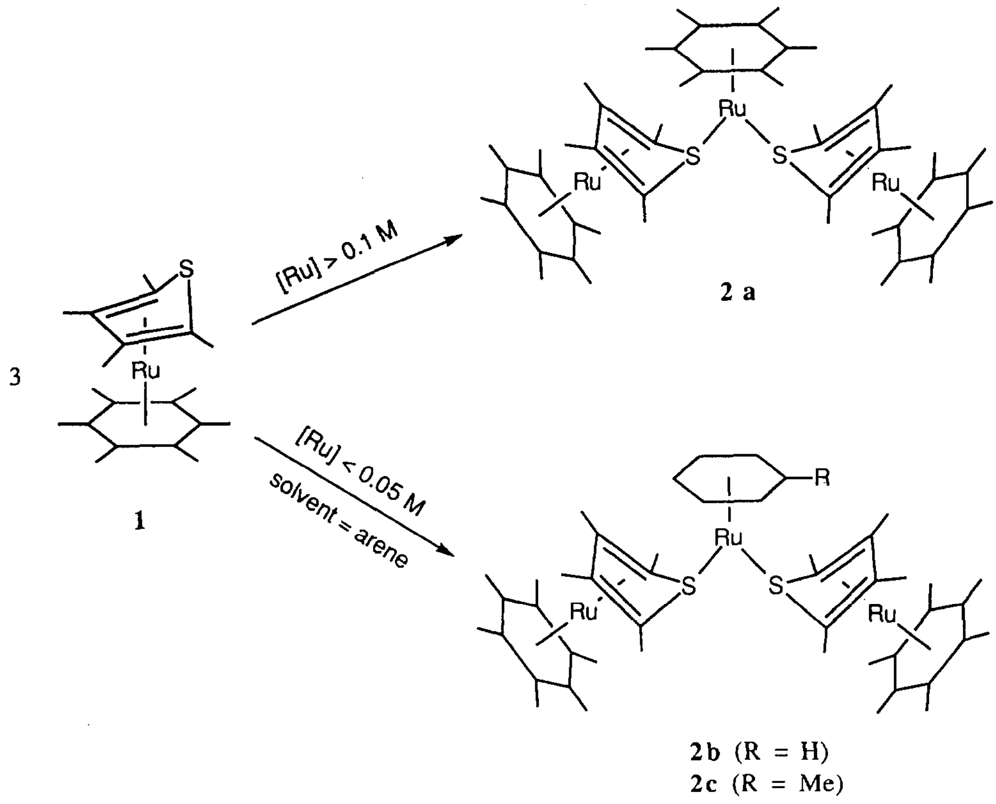
2.1. *Solution thermolysis of $(C_6Me_6)Ru(\eta^4\text{-}C_4Me_4S)$ (1)*

Solutions of **1** in hexane deposit a red orange solid upon heating at 80°C for several hours. When the reaction solution is not stirred, the product forms as strikingly large, well-formed crystals, some of which proved to be of X-ray diffraction quality. The new compound is insoluble in common organic solvents. While this might seem unusual for such a highly alkylated species, hexamethylbenzene complexes often display low solubility in our hands. Elemental analysis of the product gave the formula $(C_6Me_6)_3Ru_3(C_4Me_4S)_2$ (**2a**) while electron impact mass spectrometry (EIMS) showed a weak peak corresponding to $[(C_6Me_6)_2Ru_2(C_4Me_4S)]^+$. The decomposition of **1** in cyclohexane-d_{12} solution was followed by ^1H NMR spectroscopy. The rates were found to be first-order up to four half-lives with $k = 3.70 \times 10^{-5}\ s^{-1}$ (85°C) (eqn. (2)).

$$3(C_6Me_6)Ru(C_4Me_4S) \longrightarrow (C_6Me_6)_3Ru_3(C_4Me_4S)_2 + C_4Me_4S \quad (2)$$

2.2. *Thermal decomposition of 1 in aromatic solvents*

Thermal decomposition of a dilute C_6D_6 solution of **1** (< 0.05 M) yielded a dark brown solution whose ^1H NMR spectrum revealed the presence of free C_6Me_6, free C_4Me_4S, and a new species **2b**. A quantitative ^1H NMR study showed that free C_4Me_4S and C_6Me_6 accounted for one-third of the total hydrocarbon content in the starting **1**. At 85°C, the disappearance of **1** was found to be first order with $k = 4.04 \times 10^{-5}\ s^{-1}$, quite comparable to the rate in cyclohexane-d_{12}. When this reaction was repeated but with more concentrated solutions (> 0.1 M) we obtained **2a** at the expense of **2b**.



Scheme 1.

In contrast to **2a**, derivative **2b** proved to be soluble in benzene and toluene. Its ^1H NMR spectrum consisted of three resonances of relative intensity 3:1:1, assigned to $C_6(CH_3)_6$ and $C_4(CH_3)_4S$, respectively. The ^{13}C NMR spectrum also indicated only one type each of C_6Me_6 and C_4Me_4S ligands. At this stage, this new compound was tentatively assigned as the multidecker species [14], *e.g.* $[(C_6Me_6)Ru(C_4Me_4S)]_2Ru$. This hypothesis proved incorrect.

The results from the afore-mentioned NMR tube experiments led us to carry out the thermolysis of **1** on a preparative scale in toluene solution (> 0.1 M). From this relatively concentrated mixture, we again obtained a dark brown solution as well as a crystalline precipitate of **2a**. From the dark brown reaction solution, yellow orange crystals of **2c** were isolated. The ^1H NMR spectrum of **2c** featured three resonances of relative intensity 3:1:1 as well as a set of peaks assigned to $\eta^6\text{-}C_6H_5CH_3$. Based on these results as well as the structure of **2a**, we formulate **2b** and **2c** as $(\eta^6\text{-arene})Ru\{(C_6Me_6)Ru(\eta^4:\eta^1\text{-}C_4Me_4S)\}_2$ where arene = C_6D_6 (**2b**) or $C_6H_5CH_3$ (**2c**). Thus, arene exchange between solvent and $\eta^6\text{-}C_6Me_6$ occurs during the thermal decomposition of **1** (Scheme 1). At this stage, we recognized that the ^1H NMR spectrum of **2b** only showed signals for C_6Me_6 and C_4Me_4S because the C_6D_6 ligand is obviously unobservable by ^1H NMR spectroscopy. The ^{13}C resonance of the C_6D_6 ligand in **2b** should be a triplet due to the deuterium coupling whose nuclear spin is one. Indeed, a weak 1:1:1 triplet is observed at 73.27 ppm in its ^{13}C NMR spectrum. The arene-exchange reaction between **2c** and solvent C_6D_6 is slow at room temperature.

The solubility of **2b** allowed us to examine the redox properties of this series of compounds. A cyclic voltammetry experiment revealed a complex oxidation process commencing at ~ 350 mV (vs. Ag/AgCl). A corresponding reduction wave was not observed upon reversing the direction of the voltage sweep. In contrast, **1** undergoes reversible oxidation in two steps centered at −500 mV versus the same standard. Clearly, the redox properties of **1** are very different from its derivative **2b**.

2.3. *Structure of $(C_6Me_6)_3Ru_3(\eta^4:\eta^1\text{-}C_4Me_4S)_2$ (**2a**)*

On the basis of our crystallographic study, **2a** can be described as $(C_6Me_6)Ru\{(C_6Me_6)Ru(\eta^4:\eta^1\text{-}C_4Me_4S)\}_2$ (Fig. 1, Table 1). The molecule consists of two $(C_6Me_6)Ru(\eta^4\text{-}C_4Me_4S)$ subunits bound to a $(C_6Me_6)Ru$ center through the axial coordination of the S atoms. This structure is closely analogous to that of $(C_5Me_5)_3Rh_3(C_4Me_4S)_2$ [15]. Unlike the trirhodium complex, the $(C_6Me_6)Ru(C_4Me_4S)$ subunits are bound to the central Ru symmetrically such that they are related by a symmetry plane orthogonal to the S1–Ru2–S2 plane. The distances between the central Ru

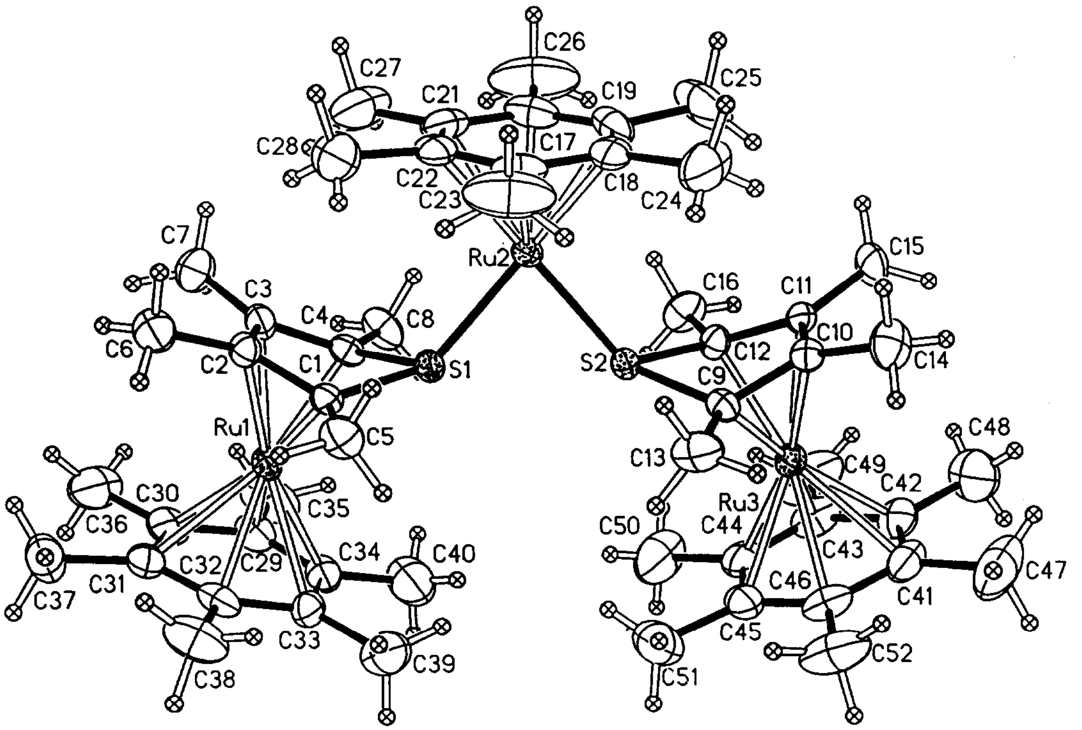


Fig. 1. ORTEP plot and numbering scheme for $(C_6Me_6)_3Ru_3(C_4Me_4S)_2$ (**2a**).

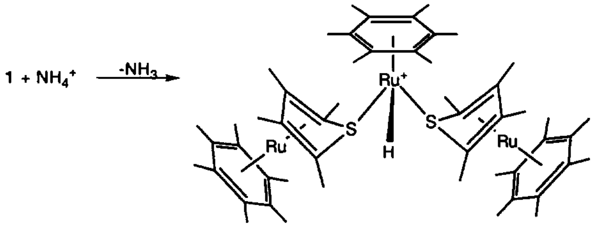
TABLE 1. Bond lengths (Å) and angles (°) for $(C_6Me_6)_3Ru_3(C_4Me_4S)_2$

Ru(1)–C(1)	2.155(7)	Ru(1)–C(2)	2.133(8)
Ru(1)–C(3)	2.140(8)	Ru(1)–C(4)	2.158(8)
Ru(2)–S(1)	2.269(2)	Ru(2)–S(2)	2.273(2)
Ru(3)–C(9)	2.134(8)	Ru(3)–C(10)	2.129(7)
Ru(3)–C(11)	2.138(8)	Ru(3)–C(12)	2.159(7)
S(1)–C(1)	1.823(8)	S(1)–C(4)	1.819(7)
S(2)–C(9)	2.819(7)	S(2)–C(12)	1.817(8)
C(1)–C(2)	1.442(10)	C(2)–C(3)	1.434(12)
C(3)–C(4)	1.431(11)	C(4)–C(8)	1.503(12)
C(9)–C(10)	1.428(10)	C(10–C(11)	1.428(11)
C(11)–C(12)	1.449(10)	C(21)–C(22)	1.392(15)
C(33)–C(34)	1.393(15)		
Ru(2)–S(1)–C(1)	122.5(3)	S(1)–Ru(2)–S(2)	78.0(1)
C(1)–S(1)–C(4)	81.6(3)	Ru(2)–S(1)–C(4)	122.6(3)
Ru(2)–S(2)–C(12)	122.5(3)	Ru(2)–S(2)–C(9)	122.9(3)
S(1)–C(1)–C(2)	112.9(6)	C(9)–S(2)–C(12)	81.0(3)
C(2)–C(3)–C(4)	108.9(6)	C(1)–C(2)–C(3)	109.5(7)
S(2)–C(9)–C(10)	113.3(6)	S(1)–C(4)–C(3)	113.8(6)
C(10)–C(11)–C(12)	108.1(6)	C(9)–C(10)–C(11)	109.8(6)
		S(2)–C(12)–C(11)	113.8(6)

atom and the S atoms of the two η^4-C_4Me_4S ligands (2.269(2) and 2.273(2) Å) are significantly longer than the corresponding Rh–S distances 2.128(6) and 2.095(6) Å in $(C_5Me_5)_3Rh_3(C_4Me_4S)_2$. This difference is a consequence of the metallic radii as well as differences in the metal oxidation states. Examples of Ru^0 thioether complexes are not available for comparison. Structurally characterized Ru^{II}–thioether complexes are not necessarily good reference species since they are hexa-coordinate. The Ru–S distances range from 2.327 to 2.377 Å in $[Ru([9]aneS_3)_2](BPh_4)_2$, and $[Ru([12]aneS_3)_2](BF_4)_2$ [16]. A comparable Ru–S distance of 2.262(1) Å is observed for the Ru–S bond *trans* to the Cl atom in the compound *cis*-$RuCl_2([14]ane\text{-}S_4)$ [17]. The S1–Ru2–S2 angle to 78.0(1)° is much more acute than the S–Rh–S angle of 92.53(8)° in $(C_5Me_5)_3Rh_3(C_4Me_4S)_2$. The metal centers in $(C_6Me_6)Ru(\eta^4\text{-}C_4Me_4S)$ subunits are sandwiched between a hexamethylbenzene ring and a butadiene plane of the $\eta^4:\eta^1$-C_4Me_4S ligand. The sum of the bond angles around the two S atoms is 326.7° for S1 and 327.4° for S2, respectively, clearly indicating the pyramidal nature of these S atoms. The S–C distances in both C_4Me_4S ligands, which range from 1.817(8) to 1.823(8) Å, are virtually the same as in $(C_5Me_5)_3Rh_3(C_4Me_4S)_2$ as are the C–S–C angles.

2.4. Protonation of $(C_6Me_6)Ru\{(C_6Me_6)Ru(C_4Me_4S)\}_2$ (2a)

Although **2a** displayed no solubility in organic solvents, its suspensions in THF dissolve upon addition of NH_4PF_6 to afford a yellow solution of [**2a**H]PF_6 (eqn. (3)).



2aH⁺

(3)

This salt dissolves in polar solvents such as CH_2Cl_2 and acetone giving air-sensitive solutions. Its FAB-mass spectrum (positive ion) consists of an peak envelope whose isotope distribution is centered at $m/z = 1172$, consistent with $[(C_6Me_6)_3Ru_3H(C_4Me_4S)_2]^+$, although the degree of protonation is not strictly obvious from FABMS data.

The room temperature ^1H NMR spectrum of **2aH⁺** is dominated by two intense peaks assigned to non-equivalent $C_6(CH_3)_6$ groups. A singlet at −11.80 ppm (1H) is assigned to the hydride ligand. Additionally, a singlet (1.11 ppm) and broad features are observed in the range 1–2 ppm. At −70°C, these features in the range 1–2 ppm develop into six sharp, equal-intensity singlets (relative intensity 3H each) and a broadened feature corresponding to intensity 6H. These are assigned to eight non-equivalent $C_4(CH_3)_4S$ groups. The very intense C_6Me_6 singlet at 2.07 ppm splits at low temperatures into two equal intensity peaks (18H:18H), but the C_6Me_6 resonance at 2.09 remained unchanged as did the hydride resonance. At 55°C, the seven $C_4(CH_3)_4S$ signals collapse to give four singlets, three of which remain broad.

The dynamics of **2aH⁺** were also probed by ^{13}C NMR spectroscopy which supports the ^1H NMR data. Focusing just on the C_6Me_6 and C_4Me_4S signals, the room temperature ^{13}C NMR spectrum of **2aH⁺** consists of three resonances assigned to C_6Me_6 plus broad features near 84 and 44 ppm. At −70°C, these broad features split to give eight signals assigned to the diastereotopic C_4Me_4S centers. At 55°C, only two C_6Me_6 resonances are observed as is a broadened signal for C_4Me_4S at 84 ppm. These observations are also consistent with hindered rotation about the Ru–S bonds. The stable rotamer is unsymmetrical. Under fast exchange conditions, the two $(C_6Me_6)Ru(C_4Me_4S)$ subunits appear equivalent.

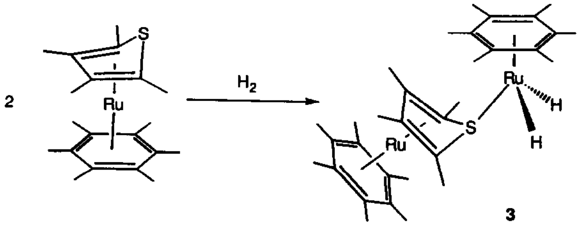
2.5. Thermolysis of 1 in the presence of hydrogen

Thermolysis of hexane solutions of **1** in the presence of H_2 afforded a yellow precipitate analyzing as $(C_6Me_6)_2Ru_2(C_4Me_4S)H_2$ (**3**). The conditions are similar to those for the conversion of **1** to **2a**. Free C_4Me_4S and a small amount of C_6Me_6 were also observed in the reaction mixture by ^1H NMR spectroscopy. Using

TABLE 2. Summary of crystallographic data for $(C_6Me_6)_3Ru_3(C_4Me_4S)_2$

Molecular formula	$C_{52}H_{78}Ru_3S_2$
Formula weight	1070.5
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	9.008(3)
b (Å)	21.987(6)
c (Å)	25.069(7)
β (°)	99.82(3)
V (Å^3)	4892(20)
Z	4
d_{calc} (g^1 cm^{-3})	1.453
Cystal dimensions (mm)	0.30×0.40×0.45
Diffractometer	Siemens P4
Radiation (Å)	λ (Mo-Kα) 0.71073
Data collection method	ω
Temperature (K)	296
Reflections measured	$\pm h$, $\pm k$, $\pm l$
Scan speed (° min^{-1})	6–20 (variable)
2Θ scan range (°)	$4 \leq 2\Theta \leq 50$
Decay	$\leq$ 2% variation
Reflection collected	9091
Independent reflections	8880 (R_{int} = 4.21%)
Observed reflections	4993 ($F > 5.0\sigma(F)$)
Absorption coefficient (cm^{-1})	10.11
Method of refinement	Full matrix least squares
$R(F)$ (%)	4.65
$R_w(F)$ (%)	5.20
Goodness of fit	1.06
Δ/σ_{max}	0.099
$\Delta\rho_{max}$ (e Å^{-3})	0.45

D_2, we also obtained **3**-d_2. Compound **3** is only sparingly soluble in benzene and toluene. Its ^{1}H NMR spectrum consists of two C_6Me_6 singlets and two C_4Me_4S singlets in the ratio 6:6:2:2. A resonance at −9.56 ppm is assigned to hydride ligands. FDMS showed a molecular ion peak with the correct isotope distribution pattern. The solid state IR spectrum of **3** shows a strong adsorption at 1873 cm^{-1}, assigned to ν(Ru–H) [18]. This band shifts to 1383 cm^{-1} in the IR spectrum of **3**-d_2. The ν(RuH)/ν(RuD) ratio is 1.35, versus the theoretical ratio 1.41. The ν(RuH)/ν(RuD) ratios for other metal hydrides ranges from 1.33 to 1.39 [19]. These data collectively support the structure of **3** as shown in eqn. (4).



(4)

3. Discussion

A complete kinetic analysis of the conversion of **1** to **2a–c** was not undertaken although a multistep process

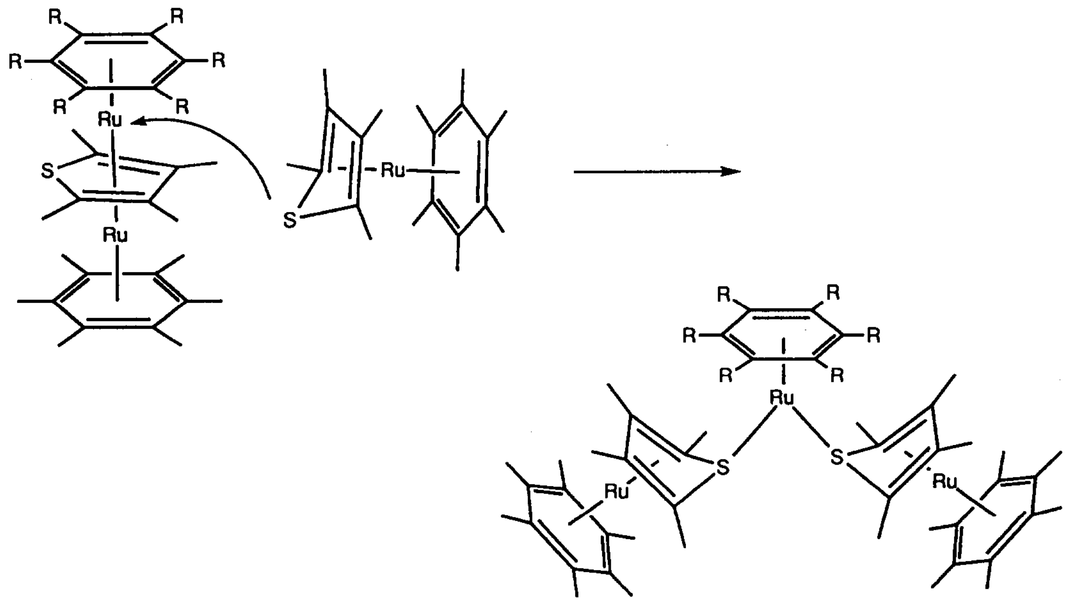


Fig. 2. Possible role of triple decker intermediates in the formation of $(C_6Me_6)_3Ru_3(C_4Me_4S)_2$ (**2a**) in $(CD_3)_2CO$ solution.

TABLE 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

	x	y	z	U_{eq} [a]
Ru(1)	574(1)	3538(1)	735(1)	34(1)
Ru(2)	3206(1)	2101(1)	2211(1)	33(1)
Ru(3)	5244(1)	3694(1)	3647(1)	34(1)
S(1)	2224(2)	2872(1)	1659(1)	34(1)
S(2)	3889(2)	2931(1)	2736(1)	34(1)
C(1)	2411(8)	2907(3)	947(3)	35(3)
C(2)	1176(9)	2620(3)	596(3)	37(3)
C(3)	−135(9)	2625(4)	850(3)	39(3)
C(4)	235(8)	2914(3)	1367(3)	36(3)
C(5)	3990(9)	2947(4)	835(3)	52(3)
C(6)	1235(10)	2352(4)	51(3)	56(3)
C(7)	−1640(9)	2352(4)	609(4)	62(4)
C(8)	−842(10)	2963(4)	1762(3)	56(4)
C(9)	5823(8)	3079(3)	3057(3)	35(3)
C(10)	6202(8)	2818(3)	3584(3)	34(3)
C(11)	4879(9)	2760(3)	3823(3)	37(3)
C(12)	3610(8)	2978(3)	3436(3)	35(3)
C(13)	6929(10)	3158(4)	2667(3)	57(4)
C(14)	7769(9)	2638(4)	3843(4)	62(4)
C(15)	4848(10)	2505(4)	4370(3)	57(4)
C(16)	1995(9)	2949(4)	3525(4)	56(4)
C(17)	4646(10)	1360(4)	1966(4)	55(4)
C(18)	4792(12)	1359(4)	2543(5)	65(4)
C(19)	3507(15)	1322(4)	2790(4)	64(4)
C(20)	2053(12)	1281(4)	2475(5)	63(4)
C(21)	1909(10)	1273(4)	1907(5)	60(4)
C(22)	3178(12)	1296(3)	1659(3)	50(3)
C(23)	5989(14)	1357(5)	1688(6)	117(7)
C(24)	6332(13)	1387(5)	2894(5)	130(7)
C(25)	3668(19)	1283(5)	3402(4)	128(8)
C(26)	654(16)	1197(6)	2722(7)	148(9)
C(27)	344(12)	1217(5)	1556(6)	117(6)
C(28)	3020(16)	1237(5)	1053(4)	106(6)
C(29)	−1056(10)	4279(4)	786(4)	54(4)
C(30)	−1237(10)	4101(4)	236(4)	57(4)
C(31)	21(12)	4098(4)	−37(4)	58(4)
C(32)	1471(11)	4253(4)	259(4)	52(3)
C(33)	1641(10)	4460(4)	807(4)	48(3)
C(34)	392(12)	4464(4)	1066(3)	54(4)
C(35)	−2423(12)	4286(5)	1054(5)	94(6)
C(36)	−2756(12)	3930(5)	−77(5)	100(6)
C(37)	−128(15)	3929(5)	−630(4)	92(5)
C(38)	2811(12)	4237(5)	−31(5)	90(5)
C(39)	3175(12)	4641(5)	1113(4)	82(5)
C(40)	595(16)	4662(5)	1650(4)	101(6)
C(41)	6815(10)	4351(4)	4160(4)	60(4)
C(42)	5532(12)	4288(4)	4393(4)	58(4)
C(43)	4090(10)	4384(4)	4064(5)	59(4)
C(44)	3955(11)	4558(4)	3519(5)	61(4)
C(45)	5242(12)	4613(4)	3276(4)	57(4)
C(46)	6669(11)	4501(4)	3593(4)	57(4)
C(47)	8390(12)	4268(5)	4489(5)	115(6)
C(48)	5668(15)	4113(5)	4983(4)	104(6)
C(49)	2705(13)	4340(6)	4322(5)	111(7)
C(50)	2403(12)	4670(5)	3191(5)	113(6)
C(51)	5054(16)	4761(5)	2685(4)	106(6)
C(52)	8085(13)	4560(5)	3342(5)	106(6)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

is indicated. The first order decomposition rates for **1** are the same in hydrocarbon and arene solvents. Nonetheless in aromatic solvents, the product distribution (*e.g.* **2a**/**2b**) is clearly concentration dependent. Our results indicate that in dilute arene solutions, the kinetically dominant nucleophile is the arene solvent itself while in concentrated solution, another molecule of **1** is relatively more favored. This argument implies that the rate constant for the cross-reaction of **1** and (arene)$Ru(C_4Me_4S)$ (arene ≠ C_6Me_6) is greater than the rate constant for the reaction of **1** with itself. This is plausible on steric and electronic grounds.

Our kinetic results can be contrasted with the thermal decomposition of $(C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S)$ which gives $(C_5Me_5)_3Rh_3(\eta^1:\eta^4\text{-}C_4Me_4S)_2$ via a bimolecular pathway. We cannot offer a satisfactory explanation for this difference. The Rh case is simpler because of the non-lability of the C_5Me_5 ligands [15]. It is noteworthy that the susceptibility of **1** to arene exchange contrasts with the robustness of $Ru(C_6Me_6)_2$ whose benzene solutions are stable to 150°C [20]. The enhanced reactivity of **1** towards ligand exchange is also manifested by its reaction with dihydrogen to give $(C_6Me_6)_2Ru_2H_2(C_4Me_4S)$.

We speculate that **2a–c** form via the triple decker intermediates (C_6Me_6)(arene)$Ru_2(C_4Me_4S)$. These species would have a $34e^-$ configuration, compatible with triple decker bonding [21]. According to this mechanism, attack of the nucleophilic sulfur center in **1** on one of the Ru centers in the triple decker would afford **2a–c** (Fig. 2). This proposal would also explain the fact that the unique arene in **2b** and **2c** is located on the central Ru atom. In the conversion of triple decker intermediate to **2b**,**c** the nucleophile (**1**) would attack the Ru bearing the less bulky and less basic arene. Conceivably the addition of H_2 to the triple decker would produce **3**. Studies are underway to test this hypothesis.

4. Experimental details

Preparative operations employed standard Schlenk techniques. Details of our experimental methods may be found in recent papers from this laboratory [9].

4.1. Synthesis of $(C_6Me_6)Ru\{(C_6Me_6)Ru(\eta^4:\eta^1\text{-}C_4Me_4S)\}_2$ (2a)

A Schlenk tube was charged with 100 mg of $(C_6Me_6)Ru(\eta^4\text{-}C_4Me_4S)$ (0.247 mmol) and 5 ml of hexane. The mixture was subjected to three cycles of freeze-pump-thaw, sealed with a Teflon stopcock under vacuum, and heated to 80°C for 25 h. Red orange crystals of **2a** grew inside the Schlenk tube. These crystals were separated from the light yellow-colored mother liquor by filtration, washed with 3 portions each of 15 ml of hexanes, and dried under vacuum. Yield: 50 mg (57%). Anal. Found: C, 58.10; H, 7.42; S, 5.67. $C_{52}H_{78}Ru_3S_2$ calc.: C, 58.34; H, 7.34; S, 5.99% X-Ray diffraction quality single crystals were grown by this method.

4.1.1. *Thermal decomposition* $(C_6Me_6)Ru(\eta^4\text{-}C_4Me_4S)$ *in* C_6D_6

A 5-mm NMR tube was charged with 12 mg of $(C_6Me_6)Ru(\eta^4\text{-}C_4Me_4S)$ (0.030 mmol) and *ca.* 0.7 ml of benzene-d_6. The solution was then subjected to three freeze-pump-thaw cycles, flame-sealed under vacuum, and heated to 85°C in a thermostated oven (*ca.* ±0.5°C) for > 20 h. The reaction progress was monitored by ^1H NMR spectroscopy. A dark brown solution was obtained. ^1H NMR analysis showed that the solution contained free C_6Me_6 and C_4Me_4S, and compound **2b**. Removal of volatiles under high vacuum gave a dark brown solid residue which was recrystallized from ~ 5 ml of hexane by cooling to −20°C. ^1H NMR (C_6D_6): 1.69 (s, 36H, C_6Me_6); 1.63 (s, 12H, β-C_4Me_4S); 1.51 (s, 12H, α-C_4Me_4S). ^{13}C NMR (C_6D_6): 92.9 ($C_6(CH_3)_6$); 82.9 (α-$C_4(CH_3)_4S$); 73.3 (1 : 1 : 1 triplets, $J(^2H\text{-}^{13}C) = 25$ Hz); 57.9 (β-$C_4(CH_3)_4S$); 15.9 ($C_6(CH_3)_6$); 13.9 (α-$C_4(CH_3)_4S$); 12.1 (β-$C_4(CH_3)_4S$).

4.1.2. *Thermal decomposition of* $(C_6Me_6)Ru(\eta^4\text{-}C_4Me_4S)$ *in toluene*

A Schlenk tube was charged with 220 mg of $(C_6Me_6)Ru(\eta^4\text{-}C_4Me_4S)$ (0.545 mmol) and 5 ml of toluene. The mixture was subjected to three freeze-pump-thaw cycles, sealed with a Teflon stopcock under vacuum, and heated to 85°C for 25 h. The red-orange crystals of **2a** were separated from the dark brown mother liquid by filtration, washed with several portions of hexane, and dried under vacuum. Anal. Found: C, 58.08; H, 7.32; S, 5.97. $C_{52}H_{78}Ru_3S_2$ calc.: C, 58.34; H, 7.34; S, 5.99%. Dark brown solid **2c** was isolated from the mother liquor after cooling to −20°C. ^1H NMR (C_6D_6) δ 5.86 (t, 4.8, 1H); 4.71 (d, 5.2, 2H); 4.63 (t, 5.2, 2H); 2.59 (s, 3H, CH_3 of toluene); 1.71 (s, 36H, C_6Me_6); 1.69 (s, 12H, β-C_4Me_4S); 1.50 (s, 12H, α-C_4Me_4S). ^{13}C NMR (C_6D_6): 92.8 (C_6Me_6); 82.8 (C_4Me_4S); 75.0 (C_6H_5Me); 73.7 (C_6H_5Me); 72.9 (C_6H_5Me); 57.8 (C_4Me_4S); 22.7 ($C_6H_5CH_3$); 15.9 ($C_6(CH_3)_6$); 13.9 ($C_4(CH_3)_4S$); 12.3 ($C_4(CH_3)_4S$).

4.3. *Synthesis of* $(C_6Me_6)Ru\{(C_6Me_6)Ru(\eta^4:\eta^1\text{-}C_4Me_4S)\}H_2$ *(3) and* $(C_6Me_6)Ru\{(C_6Me_6)Ru(\eta^4:\eta^1\text{-}C_4Me_4S)\}D_2$ *(3-d_2)*

A Schlenk tube was charged with 100 mg of $(C_6Me_6)Ru(\eta^4\text{-}C_4Me_4S)$ (0.248 mmol) and 5 ml of hexane. The mixture was subjected to three freeze-pump-thaw cycles. While frozen at 77 K, the tube was pressurized to $P = 0.516$ atm (4.08 mmol) of H_2. The tube was then sealed with a Teflon stopcock, and heated to 80°C for 18 h to give **3** as a yellow precipitate. Solid **3** was separated from the light yellow-colored mother liquor by filtration, washed with 3 × 15 ml portions of hexane, and dried under vacuum. Yield: 73 mg (88%). Anal. Found: C, 56.44; H, 7.17; S, 4.56. $C_{32}H_{50}Ru_2S$ calc.: C, 57.46; H, 7.53; S, 4.79%. ^1H NMR (C_6D_6): 2.25 (s, 18H, C_6Me_6); 1.70 (s, 18H, C_6Me_6); 1.64 (s, 6H, β-C_4Me_4S); 1.36 (s, 6H, α-C_4Me_4S); −9.56 (s, 2H, Ru-H). ^{13}C NMR (C_6D_6): 94.1 (C_6Me_6); 93.4 (C_6Me_6); 85.0 (β-$C_4(CH_3)_4S$); 52.9 (α-$C_4(CH_3)_4S$); 17.9 (C_6Me_6); 15.8 (C_6Me_6); 14.1 (α-$C_4(CH_3)_4S$); 12.5 (β-$C_4(CH_3)_4S$). FDMS: *m/e* 668 (M^+). IR (KBr): ν(Ru–H) 1873 cm^{-1}. Complex **3**-d_2 was prepared *via* the same method by using D_2 gas. IR (KBr): ν(Ru–D) 1383 cm^{-1}.

4.2. *Protonation of* $(C_6Me_6)_3Ru_3(C_4Me_4S)_2$ *(**2a**)*

To a mixture of 40.0 mg (0.0374 mmol) of **2a** and 256 mg NH_4PF_6 (1.571 mmol) was added 10 ml of THF. The mixture dissolved to give a yellow solution. After *ca.* 3 h, the volatiles were removed under vacuum, leaving a yellow solid residue. This material was extracted into CH_2Cl_2 and recrystallized by the addition of Et_2O to give yellow crystals of $[(C_6Me_6)_3Ru_2(H)(C_4Me_4S)_2]PF_6$ ([**2a**H]PF_6). Yield: 35 mg (78%). Anal Found: C, 50.28; H, 6.35. $C_{52}H_{79}F_6PRu_3S_2$ calc.: C, 51.24; H, 6.53%. ^1H NMR (CD_3COCD_3, 20°C): 2.09 (C_6Me_6, 18H); 2.07 (C_6Me_6, 36 H); 1.11 (6H); −11.80. ^1H NMR (CD_3COCD_3, −70°C): 2.092 (C_6Me_6, 18H); 2.088 (C_6Me_6, 18H); 2.07 (C_6Me_6, 18H); 2.02 (3H, Me_β); 1.93 (3H, Me_β); 1.79 (3H, Me_β); 1.73 (3H, Me_β); 1.26 (3H, Me_α); 1.11 (6H, Me_α); 1.04 (3H, Me_α). ^1H NMR (CD_3COCD_3, 55°C): 2.10 (C_6Me_6, 18H); 2.08 (C_6Me_6, 36H); 1.91 (br, 6H, Me_β); 1.84 (br, 6H, Me_β); 1.16 (br, 6H, Me_α); 1.13 (s, 6H, Me_α). ^{13}C NMR (CD_3COCD_3, 20°C): 100.8 (C_6Me_6); 96.3 (C_6Me_6); 96.3 (C_6Me_6); 16.9 (C_6Me_6); 16.2 (C_6Me_6); 14.0 (s, C_4Me_4S); 13.0 (br, C_4Me_4S). ^{13}C NMR (CD_3COCD_3, −70°C): 98.9 C_6Me_6); 94.6 (C_6Me_6); 94.2 (C_6Me_6); 84.9 (β-C_4Me_4S); 82.3 (β-C_4Me_4S); 82.1 (β-C_4Me_4S); 82.0 (β-C_4Me_4S); 47.9 (α-C_4Me_4S); 46.7 (α-C_4Me_4S); 44.8 (α-C_4Me_4S); 42.9 (α-C_4Me_4S); 15.4 (C_6Me_6); 14.9 (C_6Me_6); 14.8 (C_6Me_6); 14.4 (s, C_4Me_4S); 14.3 (s, C_4Me_4S); 14.3 (s, C_4Me_4S); 14.3 (s, C_4Me_4S); 12.7 (s, C_4Me_4S); 12.6 (s, C_4Me_4S); 12.4 (s, C_4Me_4S); 12.4 (s, C_4Me_4S); 12.1 (s, C_4Me_4S); 11.8 (s, C_4Me_4S); 11.4 (s, C_4Me_4S); 11.4 (s, C_4Me_4S); 11.3 (s, C_4Me_4S). ^{13}C NMR (CD_3COCD_3, 55°C): 101.4 (C_6Me_6); 96.8 (C_6Me_6); 84.6 (br, β-C_4Me_4S); 17.3 (C_6Me_6); 16.5 (C_6Me_6); 14.4 (s, C_4Me_4S); 14.4 (s, C_4Me_4S); 13.5 (s,

C_4Me_4S); 13.5 (s, C_4Me_4S); 13.3 (br, C_4Me_4S). FAB-MS (positive ion): m/e 1172, 669.

4.3. Crystallographic study of 2a

X-Ray crystals for compound **2a** were grown from toluene solutions and mounted on glass fibers. Data collection was performed on a Siemens P4 diffractometer with graphite monochromator (Mo-Kα, $\lambda = 0.71073$ Å). The unit-cell data were obtained from the least-squares fit of 25 reflections ($20° \leq 2\theta \leq 25°$). Crystallographic data for compound **2a** are compiled in Table 2.

Systematic absences in the data revealed the monoclinic space group, $P2_1/c$. The structure was solved by direct methods which located the Ru atoms. The remaining non-hydrogen atoms were located through subsequent difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were treated as idealized isotropic contributions (d(CH) = 0.960 Å, $U = 1.2U$ for attached C). All software is contained in the SHELXTL PLUS (4.21, 1990) program library (G. Sheldrick, Siemens (Nicolet) XRD, Madison, WI). Atomic coordinates are presented in Table 3.

5. Supplementary material available

Tables of thermal parameters, bond angles and distances, and structure factors can be obtained from one of the authors (A.L. Rheingold).

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