

Pentamethylcyclopentadienyl Ruthenium(III) vs Hexamethylbenzene Ruthenium(II) in Sulfur-Centered Reactivity of Their Thioether-Thiolate and Allied Complexes[†]

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ABSTRACT

The reactivity features of $[\text{Cp}^*\text{Ru}^{\text{III}}\{\eta^3\text{-tpdt}\}]$ (**7**) and $[(\text{HMB})\text{Ru}^{\text{II}}\{\eta^3\text{-tpdt}\}]$ (**10**) $\{\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$; $\text{HMB} = \eta^6\text{-C}_6\text{Me}_6$; $\text{tpdt} = 3\text{-thiapentane-1,5-dithiolate, S}(\text{CH}_2\text{CH}_2\text{S}^-)_2\}$ are presented, together with selected aspects of their $(\eta^3\text{-apdt})$ analogues **8** and **11** $\{\text{apdt} = 3\text{-azapentane-1,5-dithiolate, HN}(\text{CH}_2\text{CH}_2\text{S}^-)_2\}$. This account will highlight the differences observed in their reactions with metal fragments of compounds of Ru and groups 10 and 11 in various coordination environments and with alkylating agents, including α,ω -dibromoalkanes. The mechanistic pathway of the alkylation of **7** will be discussed in some detail.

I. Introduction

The chemistry of organoruthenium compounds is dominated by the occurrence of the +2 oxidation state.¹ Such compounds bearing sulfur-based ligands are of special interest, because of their relevance to biological and industrial processes.² In particular, (arene)Ru(II) complexes containing mono- and bidentate thiolate ligands are well-established. On the other hand, such complexes of monodentate thioethers, e.g., dimethyl sulfide and tetrahydrothiophene (R_2S) such as $[(\eta^6\text{-arene})\text{RuCl}_2(\text{SR}_2)]$ and $[(\eta^6\text{-arene})\text{RuCl}(\text{SR}_2)_2]^+$ (arene = *p*-cymene, 1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$, or C_6Me_6),³ are generally unstable and hence uncommon. However, Bennett and Goh have isolated stable complexes of $(\eta^6\text{-HMB})\text{Ru}(\text{II})$ containing a tridentate macrocyclic trithioether (1,4,7-trithiacyclononane, 9S3) and acyclic thiolate-thioethers, derived by base-induced fragmentation of the coordinated 9S3 ligand in **1** (Scheme 1).⁴

The literature abounds with examples of $(\text{Cp}/\text{Cp}^*)\text{Ru}(\text{II})$ complexes; however, the occurrence of analogous Ru(III) compounds is rare. The situation persists despite the convenient availability of a Ru(III) source material $[\text{Cp}^*\text{RuCl}_2]_2$ (**5**), since its first synthesis in 1984.⁵ In fact, the authors Grubbs/Bercaw, Suzuki/Moro-oka, and their

co-workers obtained mononuclear monochloro derivatives containing only Ru(II) centers from its reactions with neutral donors, like dienes and phosphines. Subsequent reactivity studies by Koelle and Hidai indicated that the +3 metal oxidation state in **5** was maintained in their dichloro⁶ and alkyl/arylthiolate-bridged⁷ derivatives only in the presence of two uninegative ligands at each Ru center. In accord with these observations, our recent results showed that **5** reacted with neutral 9S3 to give the Ru(II) monocationic species, $[\text{Cp}^*\text{Ru}(9\text{S3})]^+$ (**6**), whereas the reaction with the dianionic acyclic tpdt ligands gave a neutral $\eta^3\text{-tpdt}$ Ru(III) complex **7**,⁸ (Scheme 2). Collectively, these results illustrate the need of participation of coordinating anionic ligands for stabilization of the electrophilic $\text{Cp}^*\text{Ru}(\text{III})$ center.

We have since investigated the reactivity features of the Ru(III) complex **7** for comparison with those of its Ru(II) analogue (**10**), which we have previously obtained from $[(\text{HMB})\text{RuCl}_2]_2$ (**9**).⁹ This account will describe the different reactivities encountered in these two systems, with special reference to their function as metallodithiolate ligands toward metal fragments derived from complexes of Ru and groups 10 and 11 elements and to their electrophilic reactions, viz. protonation and alkylation.

II. $\text{Cp}^*\text{Ru}(\text{III})$ and $(\text{HMB})\text{Ru}(\text{II})$ Complexes of $\eta^3\text{-tpdt}$, $\eta^3\text{-apdt}$, and $\mu_n\text{-tpdt}$ ($n = 2$ and 3)

The complexes containing $\eta^3\text{-tpdt}$ {3-thiapentane-1,5-dithiolate, $\text{S}(\text{CH}_2\text{CH}_2\text{S}^-)_2$ } and $\eta^3\text{-apdt}$ {3-azapentane-1,5-dithiolate, $\text{HN}(\text{CH}_2\text{CH}_2\text{S}^-)_2$ } were prepared in moderate to high yields from the reaction of the μ -dichlorodiruthenium dichlorides **5** and **9** with the sodium salts of the dithiolates, as shown in Scheme 3.^{8–10}

The yield of **10** was found to vary with the relative molar proportion of the reactants, on account of its subsequent reaction with its precursor **9**. This produced the $\text{Ru}_2(\text{II,II})$ complex **12**, illustrating the high ligating capability of **10** as a bidentate donor, capable of cleaving Ru–Cl bonds, either with partial displacement of a chloro ligand in **9** (Scheme 4, route i) or without displacement of any chloro ligands, as in a similar reaction with $[(\text{COD})-$

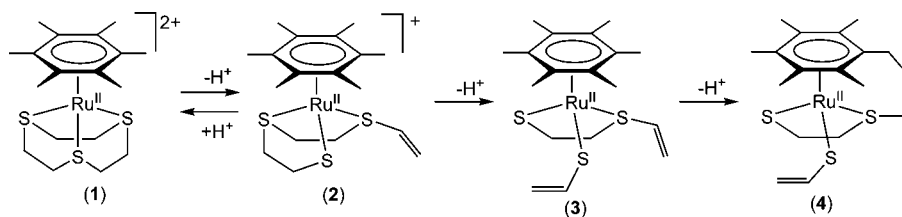
Richard Y. C. Shin was born (1978), raised, and schooled in Mauritius. He obtained his B.Sc. Honors degree (2001) in Chemistry from the National University of Singapore, followed by a Ph.D. (2005) under the guidance of Lai Yoong Goh. He is presently a Research Associate in the local Institute of Materials Research and Engineering.

Raised in Ipoh, Malaysia, Lai Yoong Goh holds a B.Sc. Honors degree from the University of Hong Kong, a M.Sc. degree from the University of Malaya, and D.Sc. and Ph.D. (with Professors Michael D. Johnson and the late Martin L. Tobe of University College London under the sponsorship of a Commonwealth Scholarship) degrees from the University of London. After a postdoctoral year with Professor J. Halpern in the University of Chicago, she served as lecturer and professor at the University of Malaya from 1968 until retirement in 1995. After 2 years in Australia as a Visiting Research Fellow at the Australian National University and Senior Research Fellow at Monash University, she came to the National University of Singapore as a Senior Fellow, and she is now a Senior Research Fellow. Her current research interests lie in the areas of organochromium and organoruthenium chemistry.

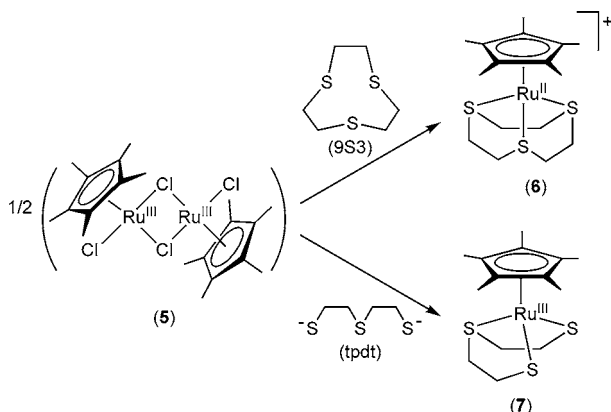
[†] This Account is dedicated to Professor Jack Halpern.

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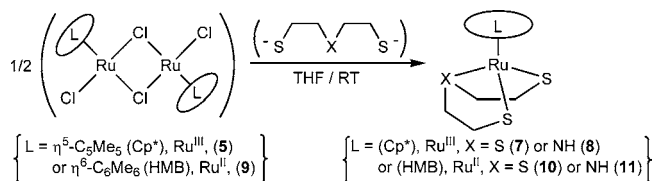
Scheme 1. Successive Deprotonation of 1



Scheme 2. Reactions of 5 with 9S3 and tpdt



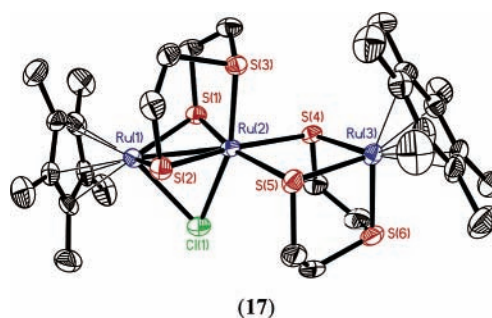
Scheme 3. Synthesis of Cp*/HMB Ruthenium Complexes of tpdt/apdt



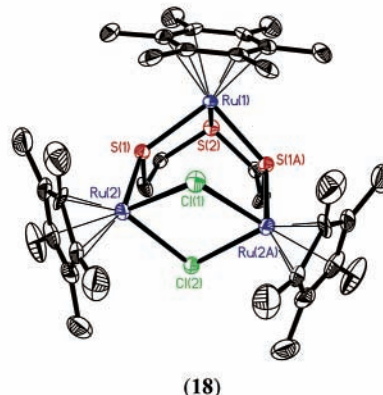
RuCl₂]_n to yield **14** (route ii). The chloro ligands in both **12** and **14** are substitutionally labile and are readily displaced by MeCN on treatment with NH₄PF₆, giving **13** and **15**, respectively.

The “cross-interaction” of **10** with μ -dichloro-Ru₂(III,III) **5**, route iii,¹¹ gave a multicomponent product mixture, containing mainly the trinuclear Ru₃(III,III,II) complex **16**.¹² Anion metathesis of this complex with NH₄PF₆ resulted in cleavage of a chloro ligand with transformation of the second into a μ -chloro bridge in a similar Ru₃ array (**17**). The minor products were another trinuclear Ru₃(II,II,II) complex **18** and a dinuclear Ru₂(III,III) complex **19**. An examination of the molecular structures and metal oxidation states of these complexes clearly reveals redox pathways in the reaction. Thus, the Ru^{III}(η^3 -tpdt) moiety present in both trinuclear **17** and dinuclear **19** must have originated from **10** via cleavage of the arene ring from its oxidized derivative. The simultaneous formation of **18** containing the “Ru-reduced” Ru₂^{II}(μ -Cl)₂ core of **5** suggests that the reaction was initiated by a redox process between **5** and **10**, resulting in oxidation of **10** to Ru^{III} with consequential labilizing and hence cleavage of its arene ring. It is proposed that the resulting highly coordinatively unsaturated and electronically deficient Ru^{III}(η^3 -tpdt) moiety then inserted into Ru–Cl bonds of a mononuclear fragment of **5** to form **19** (Scheme 5). It was observed that

19 reacted with **10** forming **16**, conceivably via nucleophilic displacement of its chloro and MeCN ligands by the thiolate S atoms of **10**. Indeed, the isolation of **19** arose from a slight fortuitous deficiency of **10**, thus preventing its total conversion to **16**. Presumably, a similar nucleophilic displacement in the reduced derivative of **5** by the thiolate S atoms of the tpdt ligand of **10** generated complex **18**.



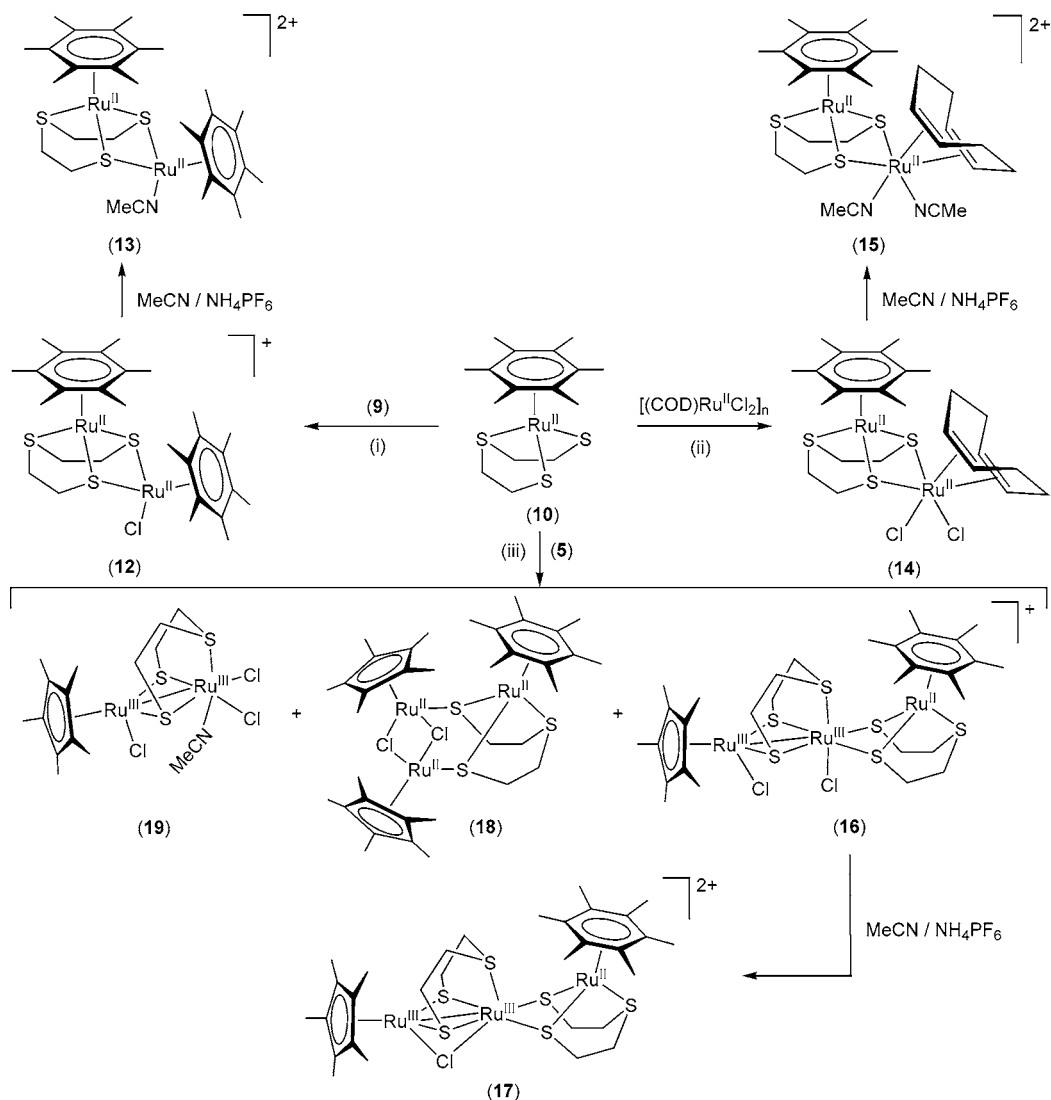
$$[\text{Ru}(1)\text{--Ru}(2) = 2.6525(7), \text{Ru}(2)\cdots\text{Ru}(3) = 3.648 \text{ \AA}; \\ \text{Ru}(1)\text{--Ru}(2)\cdots\text{Ru}(3) = 170.96^\circ]$$



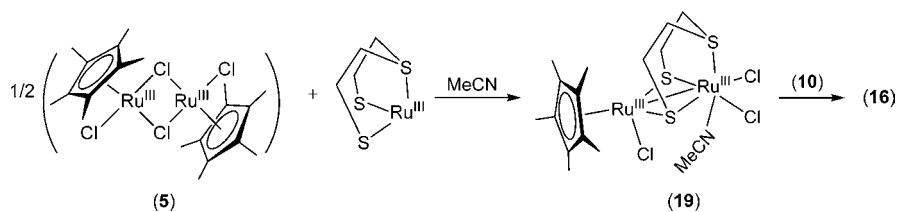
$$[\text{Ru}(1)\cdots\text{Ru}(2) = 4.291, \text{Ru}(2)\cdots\text{Ru}(2A) = 3.824 \text{ \AA}]$$

As in the case of **10**, **7** reacted with its precursor substrate **5** to give the dinuclear Ru₂(III,III) complex **20**, which contains a metal–metal bond in addition to a μ_2 -tpdt bridge (Scheme 6, route i). The “cross-interaction” of **7** with **9**, similar to that of **10** with **5**, must have involved redox-initiated pathways to form the μ -tpdt M–M bonded Ru₂(III,I or II,II) complex **21** together with other products, which unfortunately could not be isolated (route ii). The reaction of **7** with Ru(II) complexes such as [Ru(COD)-Cl₂]_n or mononuclear (PPh₃)₃RuCl₂, routes iii and iv, resulted in a Ru₃(III,II,III) complex **22**, the chloride lability of which resembles **12** and **14**, readily convertible to the solvento derivative **23** in MeCN. Trinuclear complexes

Scheme 4. Reactions of 10 with Ru(II) and Ru(III) Complexes

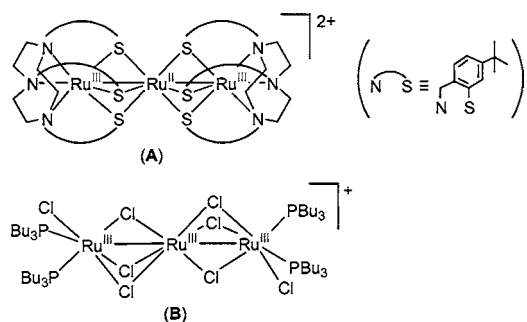


Scheme 5. Reaction Pathway for the Formation of 19 and 16



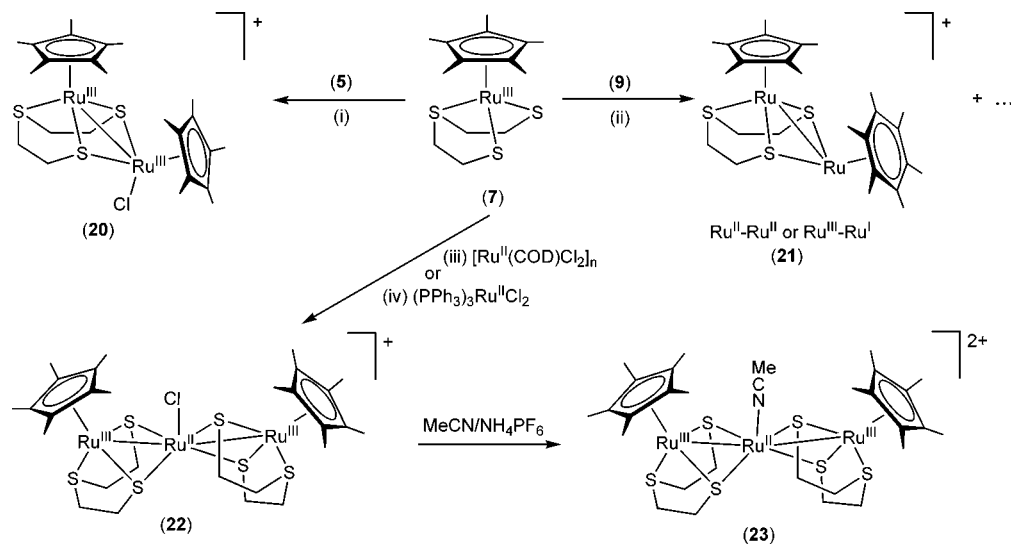
such as **16**, **17**, **22**, or **23**, in which an array of Ru centers is multiply bridged by thiolate sulfur atoms, are rare in the literature; there is only one close precedent, viz. complex **A** reported by Wieghardt,¹³ although a family of chloro-bridged complexes of Ru(III), represented by **B**, has been reported by Cotton.¹⁴

These findings show that interactions of tpdt complexes of (HMB)Ru(II) or Cp*Ru(III) with Ru complexes of like oxidation states resulted in μ_2 -dithiolate bridged dinuclear complexes. In “cross-interactions” with the precursor complexes,¹¹ the interplay of redox behavior between the reactants yielded additionally trinuclear compounds,



wherein bridging involves either two sets of tpdt ligands or one tpdt set with supporting μ_2 -chloro ligand(s). These

Scheme 6. Reactions of 7 with Ru(II) and Ru(III) Complexes

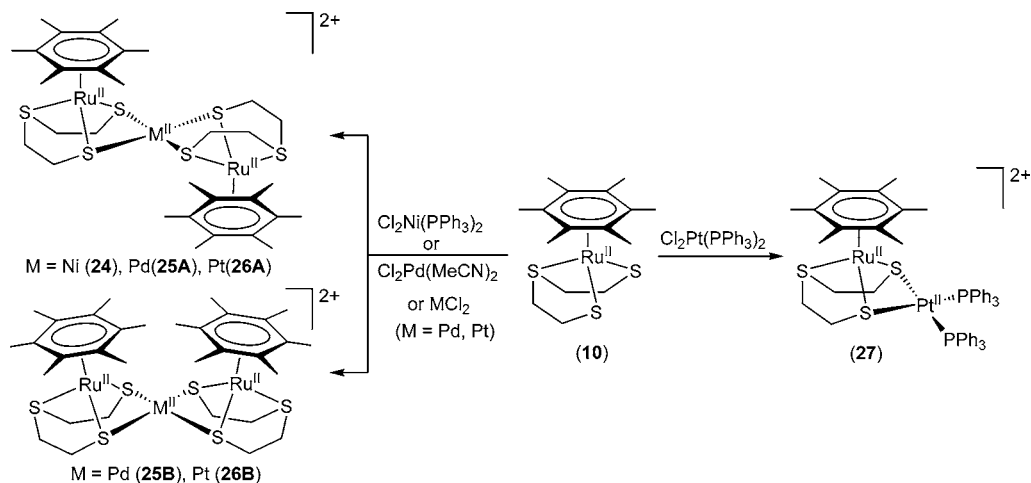


observations had stimulated an investigation of the reactivity of this trisulfur ligand in **7** and **10** toward other metal centers. This is relevant to continuing interest in heteronuclear complexes from catalytic perspectives.¹⁵

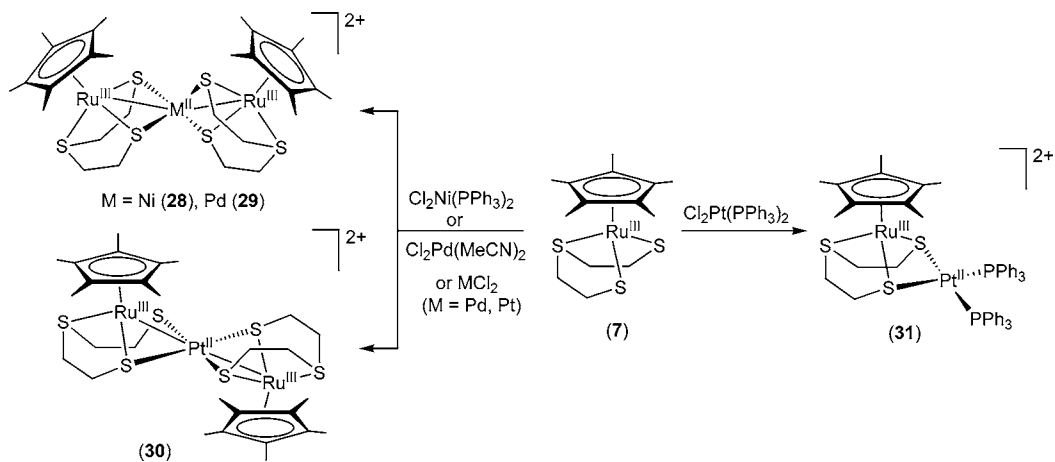
III. Formation of Bridged Heteronuclear Complexes

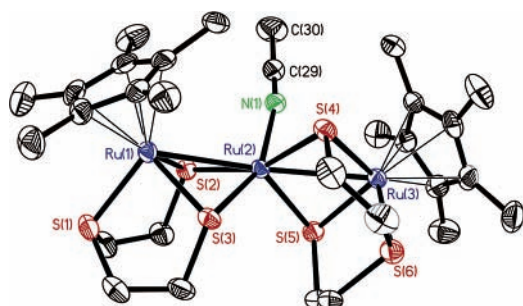
A. Complexes with Group 10 Metal Fragments. Coordination to group 10 metals was achieved by interactions

Scheme 7. Reactions of 10 with Group 10 Compounds



Scheme 8. Reactions of 7 with Group 10 Compounds

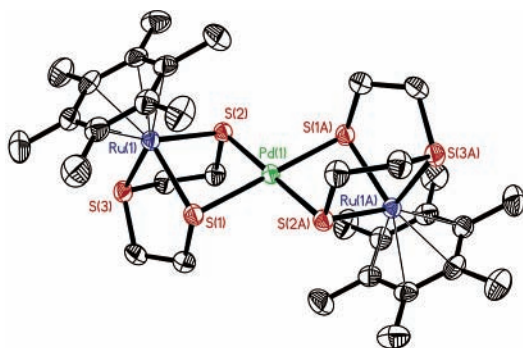




(23)

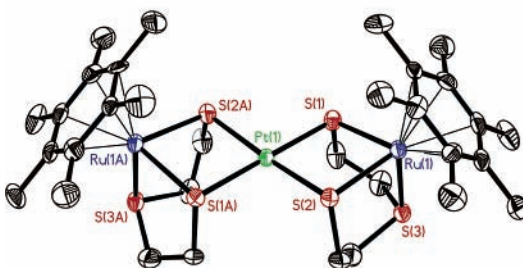
$$[\text{Ru}(1)\text{--Ru}(2) = 2.7857(5), \text{Ru}(2)\text{--Ru}(3) = 2.8160(6) \text{ \AA}; \\ \text{Ru}(1)\text{--Ru}(2)\text{--Ru}(3) = 162.54(2)^\circ]$$

with $(\text{PPh}_3)_2\text{MCl}_2$ ($\text{M} = \text{Ni}, \text{Pt}$), $(\text{CH}_3\text{CN})_2\text{PdCl}_2$, and MCl_2 ($\text{M} = \text{Pd}, \text{Pt}$) under ambient temperature conditions. Except for $(\text{PPh}_3)_2\text{PtCl}_2$, the reactions of both **10** and **7** gave as sole products the dicationic trinuclear $\mu\text{-}\eta^2\text{:}\eta^3\text{-tpdt}$ arene complexes **24**, isomers **25A/25B** and **26A/26B** (Scheme 7), and the Cp^* complexes **28–30** (Scheme 8).¹⁶ With $(\text{PPh}_3)_2\text{PtCl}_2$, the reactions gave the dinuclear analogous complexes **27** and **31**. Thus, the thiolate S atoms of **10** and **7** have acted as effective nucleophiles for the displacement of chloride or coordinated acetonitrile molecules at Pd or Pt. They are also capable of displacing PPh_3 from the coordination sphere of Ni but not of Pt, hence the formation of dinuclear **27** and **31**.



(25A)

$$[\text{Ru}(1)\cdots\text{Pd}(1) = 3.302 \text{ \AA}; \text{S}(1)\text{--Pd}(1)\text{--S}(2) = 85.20(3), \\ \text{S}(1)\text{--Pd}(1)\text{--S}(2A) = 94.80(3)^\circ]$$

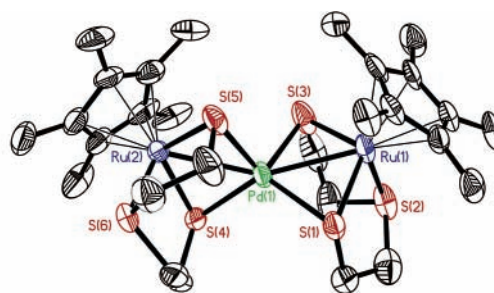


(26B)

$$[\text{Ru}(1)\cdots\text{Pt}(1) = 3.484 \text{ \AA}; \text{S}(1)\text{--Pt}(1)\text{--S}(2) = 84.39(10), \\ \text{S}(1)\text{--Pt}(1)\text{--S}(2A) = 95.64(11)^\circ]$$

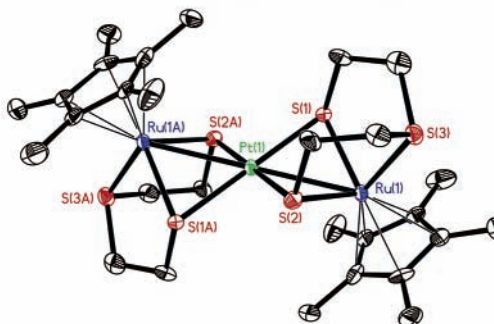
A distinctive difference in the structures of the HMB and Cp^* trinuclear complexes is the presence of metal–metal bonds in the latter, as dictated by the requirements

of the 18e rule. The (HMB)Ru–Ni complex **24** exists only in the trans isomeric form, although the Pd and Pt analogues, **25** and **26**, respectively, exist in both trans and cis forms. The molecule of the structurally determined complex **25A** possesses a center of inversion at the central metal atom, which is coordinated to four S donor atoms in a planar configuration. This configuration is also found in **27**, **30**, and **31**. Complex **30** also possesses a center of inversion at Pt, whereas in the analogous Ni (**28**) and Pd (**29**) complexes, the four S donor atoms are coordinated in a distorted tetrahedral arrangement.



(29)

$$[\text{Ru}(1)\text{--Pd}(1) = 2.6758(10), \text{Ru}(2)\text{--Pd}(1) = 2.6833(11) \text{ \AA}; \\ \text{Ru}(1)\text{--Pd}(1)\text{--Ru}(2) = 152.94(4), \text{S}(1)\text{--Pd}(1)\text{--S}(3) = 104.02(10), \\ \text{S}(1)\text{--Pd}(1)\text{--S}(4) = 117.80(10), \text{S}(3)\text{--Pd}(1)\text{--S}(5) = 109.22(12), \\ \text{S}(4)\text{--Pd}(1)\text{--S}(5) = 103.56(9)^\circ]$$



(30)

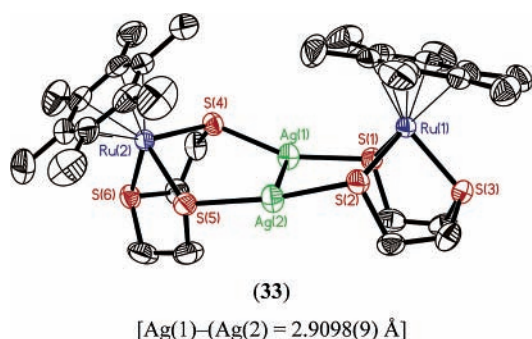
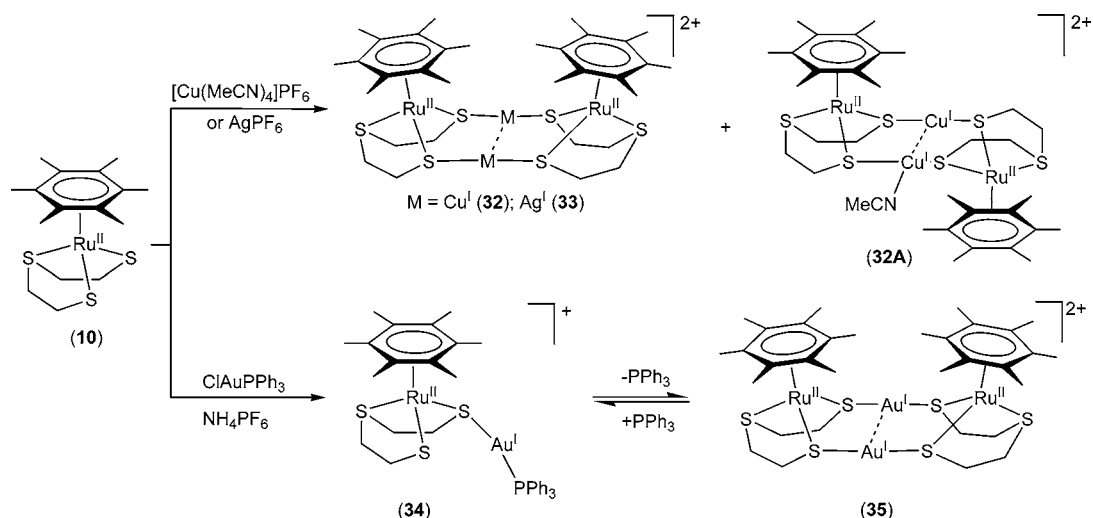
$$[\text{Ru}(1)\text{--Pt}(1) = 2.7818(12) \text{ \AA}; \text{Ru}(1)\text{--Pt}(1)\text{--Ru}(1A) = 180.00(5), \\ \text{S}(1)\text{--Pt}(1)\text{--S}(2) = 93.56(13), \text{S}(1)\text{--Pt}(1)\text{--S}(2A) = 86.44(13)^\circ]$$

B. Complexes with Group 11 Metal Fragments.

The arene Ru(II) complex **10** reacted instantaneously with $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ or AgPF_6 to give annular dithiolate-bridged diruthenium complexes of Cu(I) (**32** and **32A** in admixture) and of Ag(I) (**33**), respectively, in high yields. An apparently equally facile reaction with $(\text{PPh}_3)_3\text{AuCl}$ in MeOH in the presence of NH_4PF_6 gave a mixture of PF_6 salts of an S-“aurated” derivative **34**, and complex **35**, the Au(I) analogue of **32** or **33**. It was found that there exists an equilibrium between **34** and **35**, involving the reversible coordination of PPh_3 (Scheme 9).¹⁷

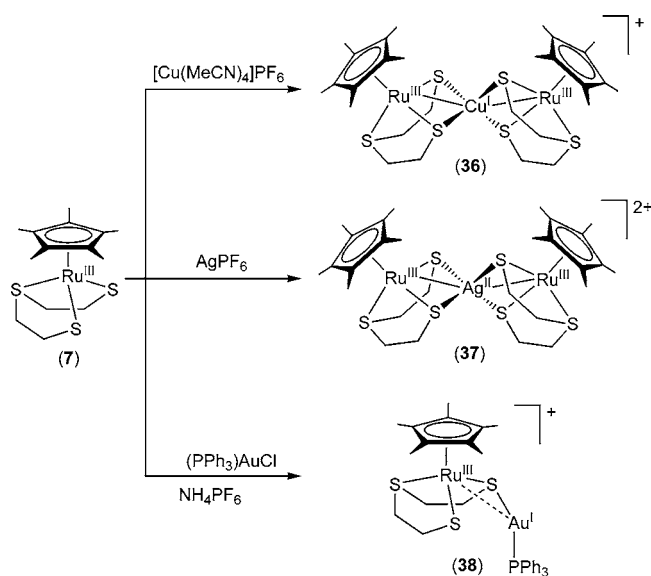
Similar reactions of the $\text{Cp}^*\text{Ru(III)}$ complex **7** gave products shown in Scheme 10. The Cu(I) and Ag(II) derivatives structurally resemble the bis(thiolate) Ru_2M derivatives of Ni(II) (**28**) and Pd(II) (**29**). The unexpected

Scheme 9. Reactions of 10 with Group 11 Compounds

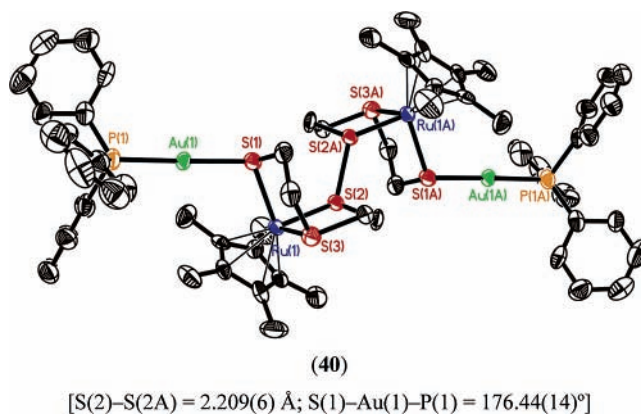


formation of the Ag^{II} complex **37**, accompanied by the formation of metallic silver, had indicated the dual role of Ag^+ as a Lewis acid in complexation and as an oxidant. The ease of oxidation of complexed Ag^{I} had precedent in the instantaneous formation of dialkyldithiocarbamate derivatives of Ag^{II} from the treatment of thiuram disulfides with a Ag^{I} salt.¹⁸ The S-aurated derivative **38** resembles the (HMB)Ru(II) derivative **34**, except for the presence of an additional weak $\text{Ru}\cdots\text{Au}$ interaction.

Scheme 10. Reactions of 7 with Group 11 Compounds



However, there is a marked difference in their reactivities. Complex **38** was found to undergo a slow conversion to the di-S-aurated complex **39** and a $\mu\text{-S}_2$ diruthenium(II) complex, **40** (Scheme 11). It is interesting to note the influence of the isolobal analogy between AuPh_3^+ and Me^+ in the formation of structures of **40** and **60** (see below).

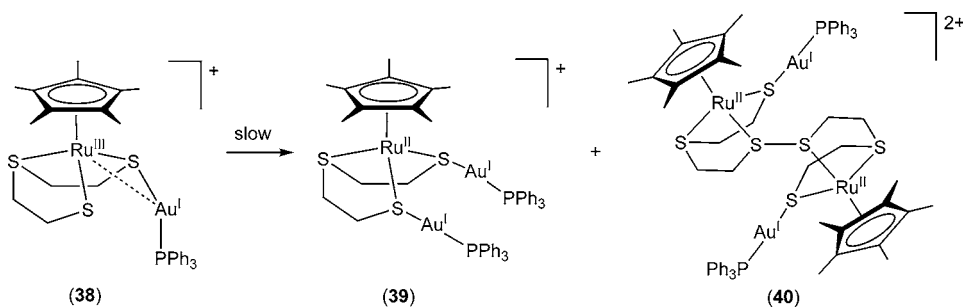


These results show that the electronic difference between (HMB)Ru^{II} and Cp^{*}Ru^{III} influences markedly the manner in their $\eta^3\text{-tpdt}$ ligand functions as a dithiolate ligand toward the group 11 metals in +1 oxidation states, resulting in derivatives of very different geometries. Thus, the dithiolate ligand at (HMB)Ru bridges in $\mu\text{-}\eta^1\text{:}\eta^1$ mode, resulting in annular tetranuclear Ru_2M_2 derivatives, the solid state structures of which show metalophilicity between the group 11 metals. In comparison, $[\text{Cp}^*\text{Ru}^{\text{III}}(\eta^3\text{-tpdt})]$ behaves as a metalodithiolate chelate toward bare Cu^{I} and Ag^{II} centers, yielding cationic (bis)- η^2 -dithiolate metal–metal bonded Ru_2M derivatives but coordinates as a monothiolate ligand to AuPPh_3 ; this mono-S-aurated Ru(III) complex undergoes a slow conversion to a di-S-aurated Ru(II) derivative together with a $\mu\text{-S}_2$ diruthenium(II) species.

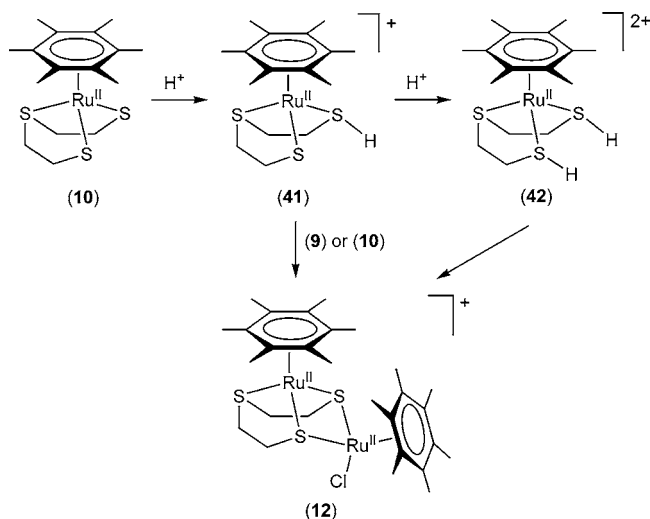
IV. Electrophilic Reactions

A. Protonation. Treatment of **10** with 1–2 mol equiv of HCl or HPF_6 resulted in instantaneous protonation of one

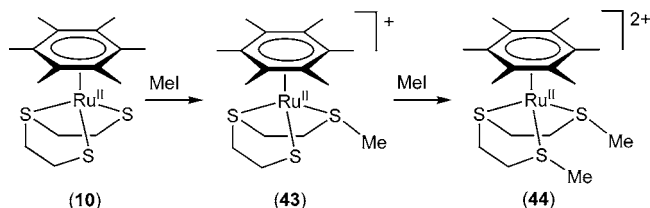
Scheme 11. Transformation of 38 in Solution



Scheme 12. Protonation of 10



Scheme 13. Methylation of 10



of its thiolate S donor atoms, producing the cationic species **41**, which reacted with **9** or **10** to yield **12**. A large excess of acid (>60 mol equiv) was required for complete diprotonation to the dicationic species **42**, which was very unstable in less acidic solution, readily converting to **12** (Scheme 12).⁹ Similar protonation of **7** led to unstable products, which appeared to revert to **7**.

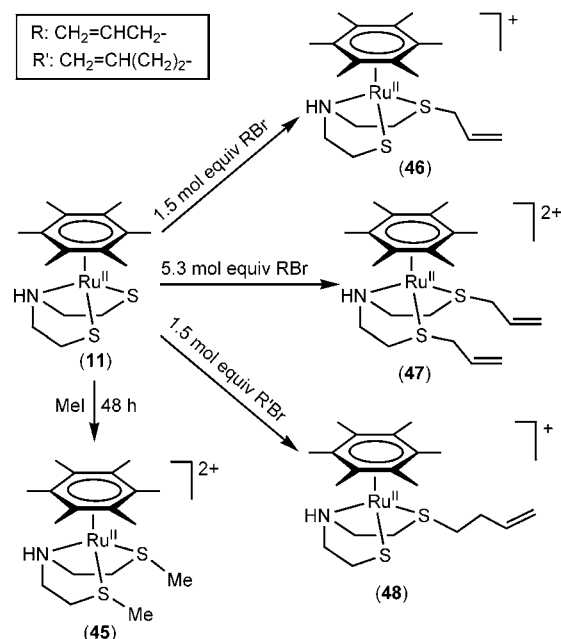
B. Alkylation. i. Alkylation of (HMB)Ru(II) Complexes.

One of the salient reactivity features of thiolate complexes is their ability to undergo S-alkylation. In this system, this was borne out by the reaction of **10** with a stoichiometric amount of MeI to give **43**, which reacted further with a large excess of MeI in a less facile reaction to give **44** (Scheme 13).⁹

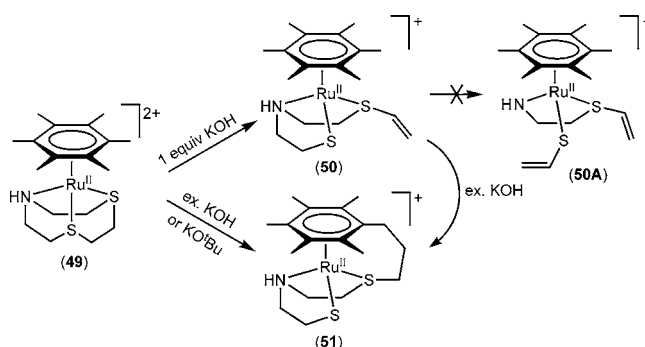
Likewise, the apdt complex **11** underwent dialkylation with excess MeI to give **45**.¹⁰ With bromoalkenes, mono- and bis-S-alkylation could be achieved, as found in complexes **46**–**48** (Scheme 14).

The S-vinyl complex **50** was derived by base-initiated S–C bond cleavage of a coordinated NS₂ macrocyclic

Scheme 14. Alkylation of 11 with Mel and Bromoalkenes

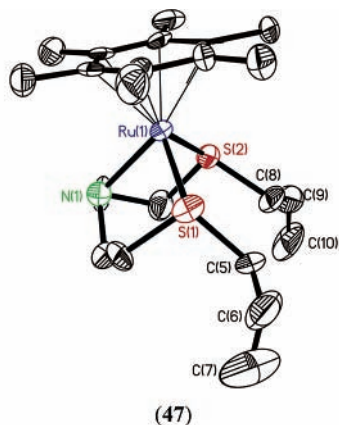
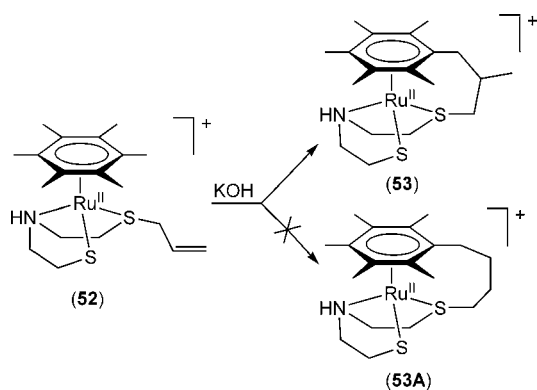


Scheme 15. Deprotonation of 49

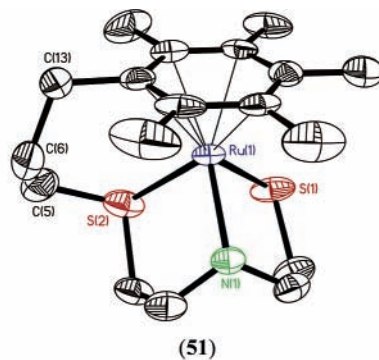


ligand in **49** (Scheme 15). Such S–C cleavages are well-documented in thia macrocyclic ligands in complexes of Ru¹⁹ and group 9 metals.²⁰ In particular, these reactivity features bear direct relevance to those previously observed by Bennett and Goh for the 9S3 analogue (**1**) (Scheme 1),⁴ except that in this present case a second deprotonation step to give **50A** is not feasible. It appears that S–C cleavage cannot occur in the NH(CH₂)₂S linkages of **49**. However, as in **1**, further deprotonation can occur at a Me substituent of HMB, giving rise to the tethered species **51** via an intramolecular Michael addition of the resulting carbanion to the terminal ethene carbon of the thioether

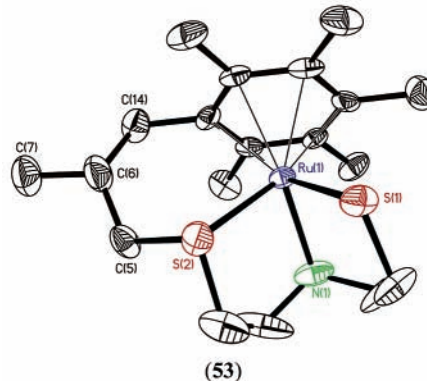
Scheme 16. Base-Promoted C–C Bond Formation



[C(5)–C(6) = 1.49(3), C(6)–C(7) = 1.26(4),
C(8)–C(9) = 1.45(3), C(9)–C(10) = 1.31(4) Å]



[Ru(1)–S(1) = 2.385(2), Ru(1)–S(2) = 2.343(2),
Ru(1)–N(1) = 2.160(7) Å]



[Ru(1)–S(1) = 2.3817(15), Ru(1)–S(2) = 2.3270(16),
Ru(1)–N(1) = 2.141(5) Å]

vinyl appendage. A similar deprotonation in **52** led to **53** containing a SC₃ tether “strap” as in **51**, to the exclusion of the formation of a SC₄ tether as in **53A** (Scheme 16).

Treatment of these alkenyl complexes with acid results in instantaneous protonation at the thiolate donor atom. In the case of the S-vinyl complex **50**, this is followed by a slow rearrangement to generate mainly the original macrocyclic complex **49**, together with an isomer **50B** as a minor product (Scheme 17).

Dialkylation of *cis*-thiolates by α,ω -alkyl dihalides has been developed by Busch as a convenient route for “ring closure” in the formation of thioether macrocycles at Ni(II) centers.²¹ Thus, Sellmann had applied the method for a high-yield synthesis of 9S3 via a Mo(9S3) complex²² and Darensbourg²³ had used it extensively for the synthesis of macrocyclic N₂S₂ and N₃S₂ donor ligand sets via precursor complexes at Ni(II), Co(II), and Rh(III). In similar studies, we have prepared several mesocyclic (arene)Ru(II) complexes of the zS3 type from **10**, viz. **54**, **1**, and **55–57** for $z = 8–12$, respectively,⁹ and of the zNS₂ type from **11**, viz. **49**, **58**, and **59** for $z = 9–11$, respectively (Scheme 18).¹⁰ The latter complexes constitute the first η^6 -arene metal complexes of the zNS₂ macrocyclic ligands.

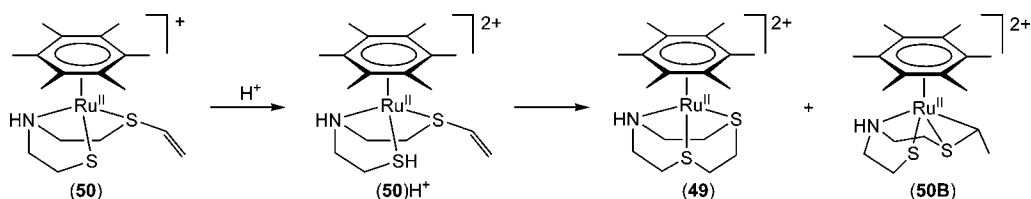
To date, such compounds of 9NS₂ (**49**) and 10NS₂ (**58**) are rare, on account of the difficulty encountered in the

synthesis of the ligands.²⁴ Thus, this methodology provides a viable route to complexes of macrocyclic aza-dithia ligands.

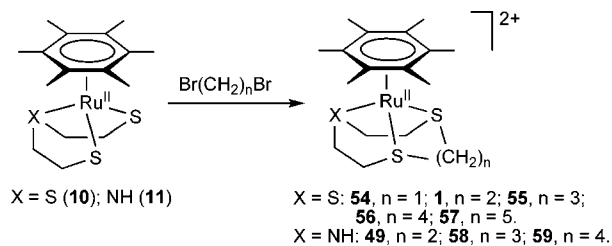
ii. Alkylation of Cp*Ru(III) Complexes.²⁵ Treatment of the Ru(III) complex **7** with MeI or (Me₃O)BF₄ led to an entirely unexpected outcome. There occurred alkylation at one S atom and S–S coupling at the other, yielding the Ru(II) complex **60** as the predominant product, with the di-S-alkylated complex **61** as a minor product (Scheme 19). The S(ethyl) and the apdt analogues, **60_{Et}** and **60_{SNS}**, respectively, were similarly obtained. Such instances of alkylation-induced S–S coupling had not been observed before. Previous work of Taube, Rauschfuss, Puerta, and others has established that disulfide bond formation in coordination and organometallic compounds, as well as in many protein molecules, is brought about by oxidative coupling.²⁶

The comparable efficiency of MeI or (Me₃O)BF₄ in the transformation of **7** to **60** suggests that the reaction must have been initiated by electrophilic attack of Me⁺ on a thiolate sulfur of **7**. This would generate racemic Ru(III) intermediates (*R*)-**60A'** and (*S*)-**60A'**. An internal electron transfer (IET) in these then led to the respective cationic Ru(II) sulfur-centered radicals (*R*)-**60A** and (*S*)-**60A**; coupling of these thiyl radicals would then give two pairs of S–S-bonded dinuclear diastereomers, detectable in the proton NMR spectrum of **60** (Scheme 20). However, only the *RS*- and *SR*-enantiomeric pair of species **60** had been

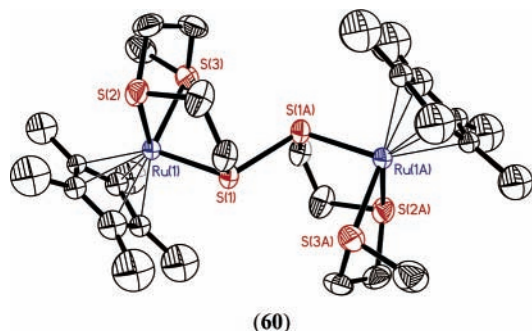
Scheme 17. Acid-Promoted C–S Bond Formation



Scheme 18. Ring Closure with Dibromoalkanes



crystallized out and hence characterized crystallographically. Such metal thiyl radicals, formed via oxidation of metal thiolates, had been invoked as intermediates in the formation of coordinated disulfides by Sullivan²⁷ and Grapperhaus,²⁸ and of a tris-disulfide bridged diruthenium complex by Wieghardt.¹³

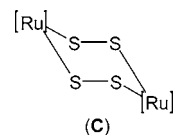


[Ru(1)–S(1) = 2.2813(17), Ru(1)–S(2) = 2.3261(18),
Ru(1)–S(3) = 2.3702(19), S(1)–S(1A) = 2.194(3) Å]

The radical nature of this reaction was established via reactions of **7** with methylating reagents in the presence of acrylonitrile (AN), a strongly electrophilic alkene known to react readily with thiyl and other noncarbon radicals.²⁹ It was found that in the presence of a 10-fold excess of AN, an AN adduct **62**, in which Ru(II) is coordinated to a cyano-substituted 9S3 ligand, was an additional product in substantial proportion, while the relative yield of the disulfide **60** varied with solvent and the nature of the alkylating agent, on account of its subsequent facile reaction with **7** (discussed below).

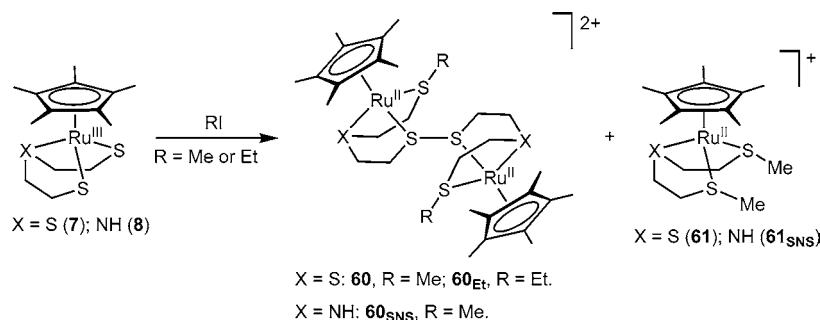
Complex **62** was the sole product from the reaction of **7** with I_2 in the presence of AN. In the absence of AN, the instantaneous reaction of **7** with I_2 led to the isolation of $\{\mu\text{-}\eta^6\text{-}(\text{S}(\text{CH}_2\text{CH}_2\text{S})_2)_2\text{Ru}_2\}$ complex **63**, in high yield (Scheme 21). On the basis of electrochemical evidence, the transformations are envisaged to go via a Ru(IV) species **IIA**, which underwent intramolecular electron rearrangement to generate a Ru(III) S-centered radical **IIB**. In the presence of AN, the S-centered radical **IIB** was effectively

trapped to form the AN adduct **62**. We note that Grapperhaus lately reported a similar carbon–sulfur bond formation between a Ru(III) thiyl radical and the enol tautomer of acetone.³⁰ In the absence of AN, **IIB** dimerizes to form **IIIA**. A repeat intramolecular electron arrangement then gives the Ru(II)–Ru(II) diradical **IIIB**, which undergoes a second S–S coupling to give species **63**. The molecular structure of **63** possesses a centrosymmetric Ru_2S_4 core with the two Ru centers in a trans configuration, reminiscent of a similar $[\text{Ru}]_2\text{S}_4$ moiety (**C**) ($[\text{Ru}] = [(\text{MeCp})\text{Ru}^{\text{III}}(\text{PPh}_3)]$) obtained by Rauchfuss.³¹ Alternatively, twice coupling of the S radical of **IIB** with a lone pair on the thiolate S of a second unit of the same moiety would generate simultaneously two $2c/3e$ S–S bonding species **IIIC**. Such $(\sigma)^2(\sigma^*)^1$ odd-electron bonds are a common type of bond in heteroatom-centered radicals and radical ions.³² The higher energy electron in the σ^* orbital of this bond would readily be transferred to the Ru centers giving the Ru(II)–Ru(II) species **63**.

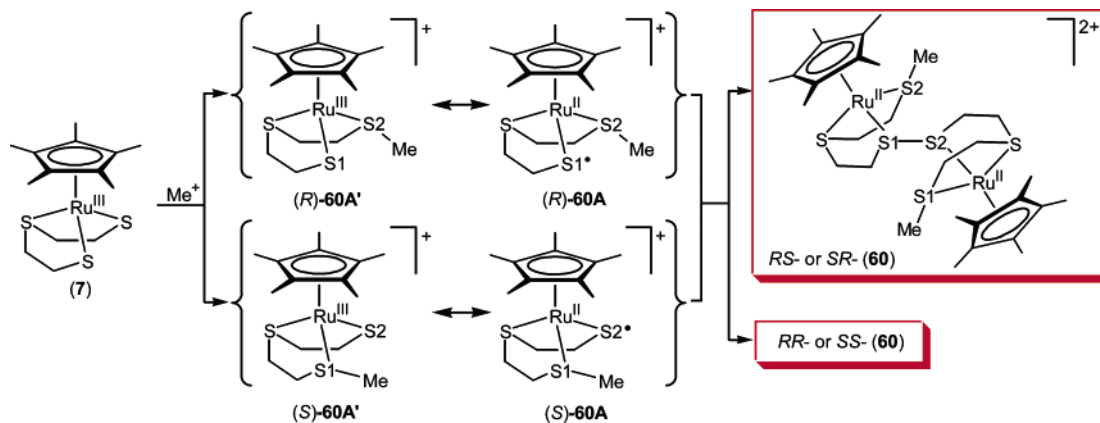
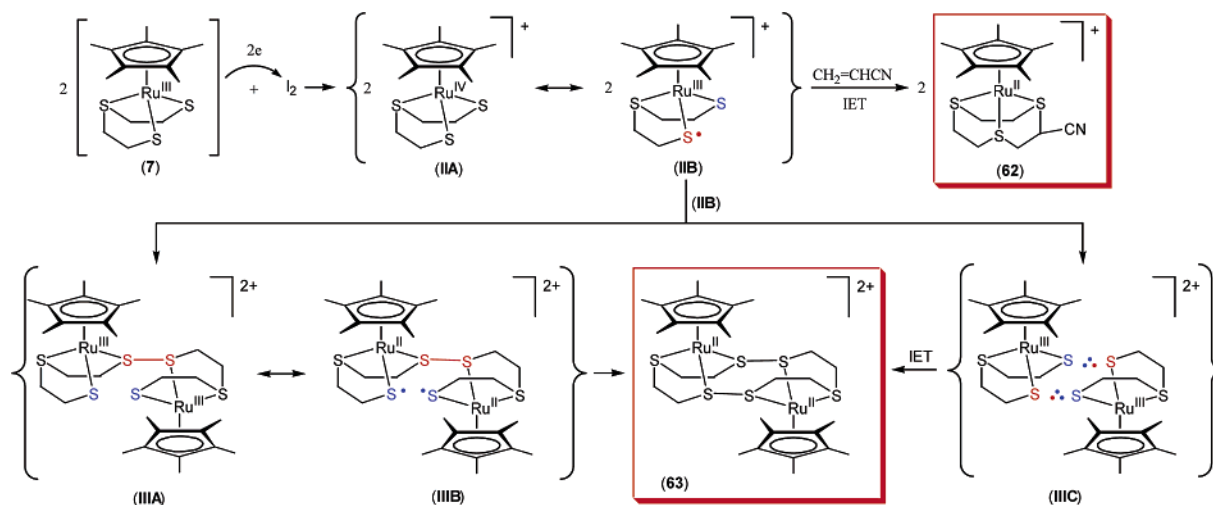


The interaction of **60** with **7** arises from its facile reversible dissociation into the mononuclear cation radical **60A** (Scheme 22). This dissociation is supported by evidence from a combination of electrochemical, EPR, UV–vis, and NMR experiments. Some of the reactivity features of **60A** are summarized in Scheme 23. Thus, it reacted as a radical initiator with ${}^n\text{Bu}_3\text{SnH}$, abstracting the radical ${}^n\text{Bu}_3\text{Sn}^\bullet$ to form the RuSSnBu_3 -containing complex **64** (route a). In the reaction with sodium naphthalide (route b), an electron reduces **60A**, generating complex **65**, which was isolated and readily alkylated to give **61**. The interaction of **60A** with **7** (route c) had led to isolation of the dinuclear species **66**. The observed second-order kinetics of this reaction, first-order in each reactant, are consistent with a rapid mononuclear–dinuclear preequilibrium (Scheme 22), followed by a slower reaction of **60A** with **7**. It was proposed that this involves the formation of an intermediate **IV** via coupling of the S-centered radical in **60A** and the S lone pair of **7** to give a $\text{S1}\cdot\text{S4}$ ($2c/3e$) disulfide bond. As in **IIIC** (Scheme 21), the transfer of the σ^* electron in this bond to Ru(III) resulted in a Ru(II) center and the S1–S4 bond formation; complex **66** would finally be formed via a concomitant or subsequent intramolecular nucleophilic attack of thiolate S6 on the other Ru(II) center, resulting in displacement of the ligated S3Me

Scheme 19. Alkylation of 7 and 8



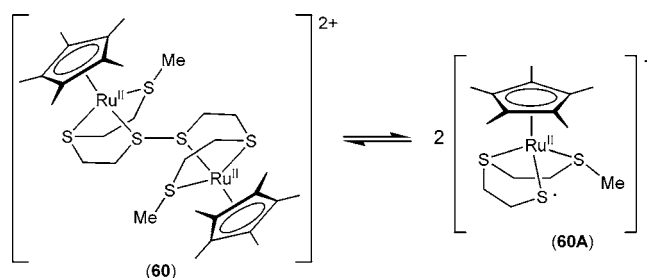
Scheme 20. Mechanistic Pathway for the Formation of 60

Scheme 21. Redox Interaction between 7 and I₂

moiety, the step to the (CH₂)₂S3Me pendant chain at S2 (route c1). Simultaneously, the weak S1...S4 bond in IV could undergo reversible cleavage to the S4-centered radical IIB and species 65 with a lone pair electron at S1 (route c2); in essence, this constitutes an inner sphere transfer of an electron from 7 to 60A. The interaction of IIB and 65 with AN and MeI, respectively, then gave the isolated species 62 and 61. In the presence of MeI alone, it is highly likely that IIB would be converted via a radical pathway to species 60A, which on dimerization would regenerate 60.

The above findings show that while sulfur alkylation of the ligand at (HMB)Ru(II) gave conventional S-alkylated

Scheme 22. Reversible Dissociation of 60 in Solution



derivatives that at Cp*Ru(III) had initiated an internal electron transfer, resulting in the formation of a thiyl radical, the precursor to a S-S bond which is susceptible

Ru(II)/Ru(III) and groups 10 and 11. Although both complexes behave as dithiolate chelates in bridging mode, dihomonuclear derivatives are formed with Ru fragments of like oxidation state, whereas trihomonuclear complexes derive from interactions with Ru complexes of different metal oxidation states. The triheteronuclear Ru_2M complexes containing "bare" M(II) centers of group 10 are formed in both (HMB)/Cp**Ru* systems, but those containing "bare" Cu(I) and Ag(II) centers of group 11 are found only for the Cp**Ru* system. For the (HMB)Ru(II) system, the tpdt ligand coordinates in $\mu\text{-}\eta^1\text{:}\eta^1$ mode, giving rise to annular tetranuclear Ru_2M_2 complexes. In all of these derivative compounds, the +3 metal oxidation state at Cp**Ru* is maintained, attesting to the efficacy of the dithiolate ligand in the stabilization of Ru(III).

In contrast to thiolate alkylation at (HMB)Ru(II), that at Cp**Ru*(III) initiates a rich S-centered reactivity, which arises from several subsequent processes, viz. internal electron transfers, coupling of thiyl radicals, and a facile reversible homolytic dissociation of the ensuing S–S bond. This study has provided mechanistic insights, which are relevant to current interest in the nature of (i) S-alkylation/S-dealkylation in desulfurization processes² and methyl transfers in biological processes³⁴ and (ii) the roles of thiolates, disulfides, and thiyl radicals in many protein functions.³⁵ Ring closure of the η^3 -tpdt/ η^3 -apdt ligands in the Ru complexes with α,ω -dibromoalkanes was easily effected to give trithia or azadithia macrocyclic derivatives as the sole product in the (arene)Ru(II) system but in admixture with a redox-initiated derivative in the Cp**Ru*(III) system.

It is appropriate to point out here that any apparently complex features in Cp**Ru*(III) chemistry should not be underestimated, as they may well yield surprisingly new findings. It may also be noted that this area of Cp**Ru*(III) chemistry remains largely unexplored and much can be done with modifications of the η^3 -tpdt and η^3 -apdt to include selected permutations of O, S, Se, and N for donor atoms, functionalizing of N in η^3 -apdt, as well as the use of tripodal thiolate ligands.

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