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Review

Towards novel organic synthesis on multimetallic centres: syntheses and reactivities of dinuclear ruthenium thiolate complexes

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Abstract

From the reactions of [Cp*RuCl(μ_2-Cl)$_2$RuCp*Cl] (Cp* = η^5-C_5Me_5) with thiolate compounds, four types of thiolate-bridged diruthenium complexes have been obtained depending upon the thiolate source. These diruthenium complexes serve not only as a potential precursor for the synthesis of dinuclear disulfide-thiolate complexes and mixed-metal sulfide-thiolate clusters but also provide unique bimetallic reaction sites for the activation and transformations of various substrates such as alkynes, organic halides and H_2.

Key words: Ruthenium; Thiolate; Alkyne; Cluster; Metallacycle; Oxidative addition

1. Introduction

The chemistry of complexes containing more than two transition metals has been progressing rapidly in recent years. The importance of di- and polynuclear complexes stems not only from their intriguing structural diversity and physical properties but also from their potential to provide the reaction site for unique organic transformations. The latter feature results from the generation of a highly activated substrate molecule at the multimetallic site which is not accessible at the monometallic centre. Several reviews of the significant advances in reactions promoted by transition metal carbonyl clusters have recently appeared [1–6]. In contrast, the reactions which proceed on the multimetallic sites containing sulfur ligands have been relatively less explored [7], because, at least in part, sulfur ligands have long been believed to poison the reactivities of the metal species due to strong coordination to possible reaction sites. However, the presence of firmly bound sulfur bridging ligands may rather be of value in preventing the multimetallic core from fragmentation under drastic reaction conditions, which is frequently observed for the metal clusters formed only by relatively weak metal–metal bonds. In this article, we will describe the chemistry of thiolate-bridged diruthenium complexes developed recently in this laboratory. Emphasis will be put upon the transformations of organic substrates at the dinuclear sites, where the bridging thiolate ligands play an important role in retaining the dinuclear structure throughout the reaction.

2. Preparation of thiolate-bridged diruthenium complexes

Transition metal thiolate complexes have long been the subject of intensive study [8,9]. This interest mainly arises from the relevance of these compounds to the active sites of certain biological systems and this has led to the synthesis of a great number of thiolate complexes containing the metals involved in these systems. In contrast, the chemistry of metal thiolates not relating to biological systems has been relatively less strongly developed. Thus, compared with the extensive studies associated with Fe thiolate compounds [10], those of Ru have been left unexplored, although this is an important metal in organic synthesis.

Stimulated by the discovery of a convenient method for synthesizing a half-sandwich Ru complex [Cp*RuCl(μ_2-Cl)$_2$RuCp*Cl] (**1**, Cp* = η^5-C_5Me_5) [11–14], we have investigated the reactions of **1** with various thio-

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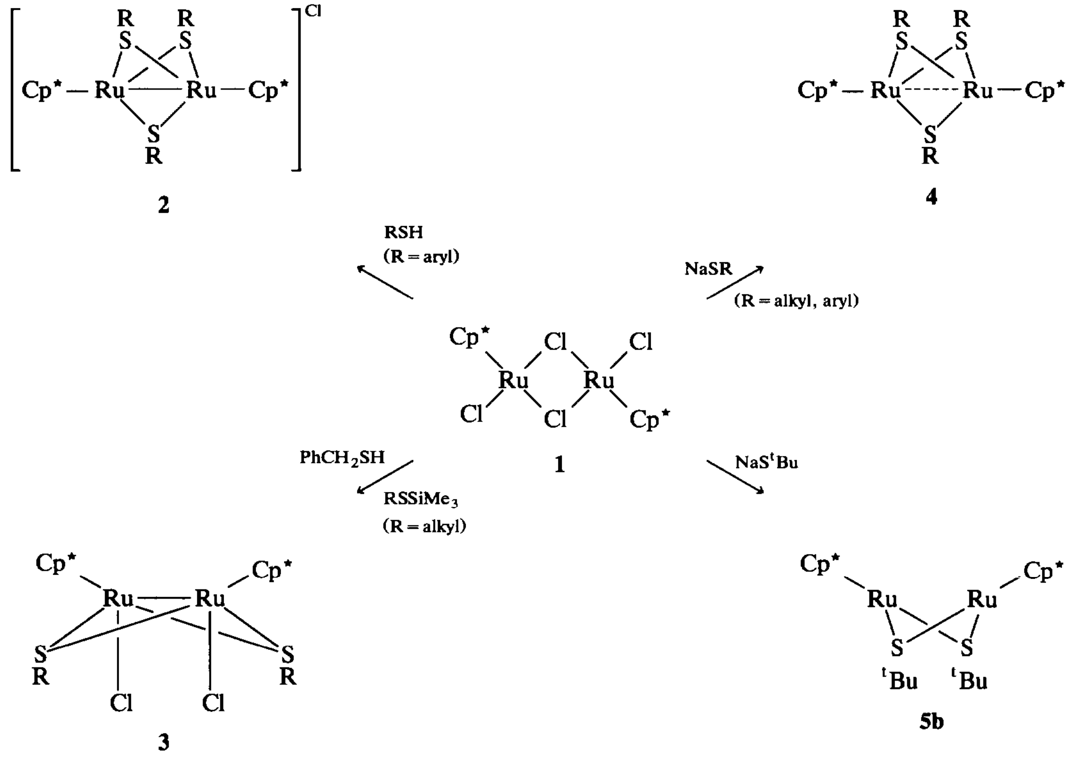
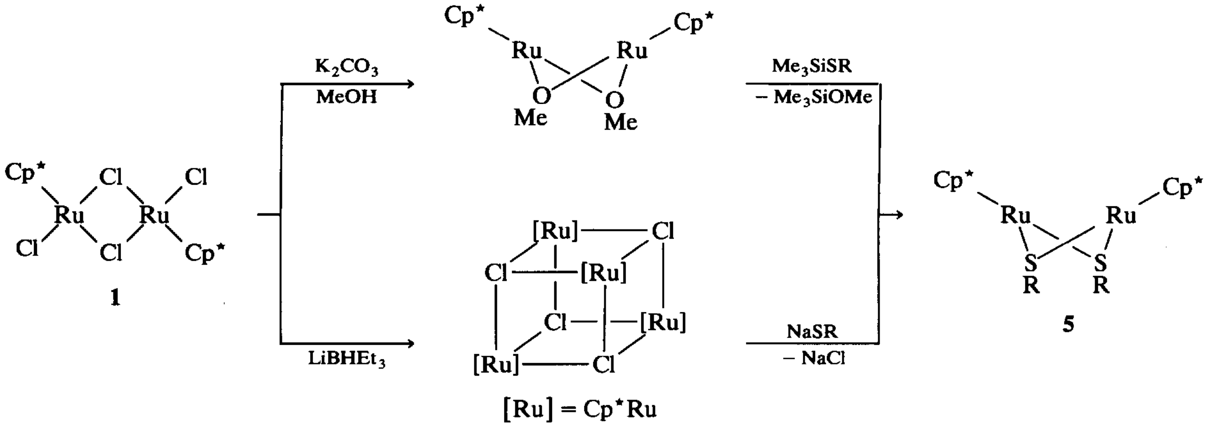


Scheme 1.

late compounds in detail. This has led to the isolation of four types of thiolate-bridged diruthenium complexes as depicted in Scheme 1. Thus, treatment of **1** with excess arenethiols in CH_2Cl_2 at room temperature resulted in the formation of cationic Ru^{III}/Ru^{III} complexes with three thiolate bridges, $[Cp^*Ru(\mu_2\text{-}SR)_3RuCp^*]Cl$ (**2**; R = aryl), whereas the reaction of **1** with $PhCH_2SH$ under similar conditions afforded a neutral Ru^{III}/Ru^{III} complex bridged by two thiolate ligands, $[Cp^*RuCl(\mu_2\text{-}SCH_2Ph)_2Ru(Cl)Cp^*]$ (**3b**) [15–17]. Alternatively, complexes of this type, $[Cp^*RuCl(\mu_2\text{-}SR)_2Ru(Cl)Cp^*]$ (**3**; R = alkyl), proved to be prepared more generally upon treatment of **1** with excess $RSSiMe_3$ in THF at reflux [16,17]. Despite the pres-



Scheme 2.

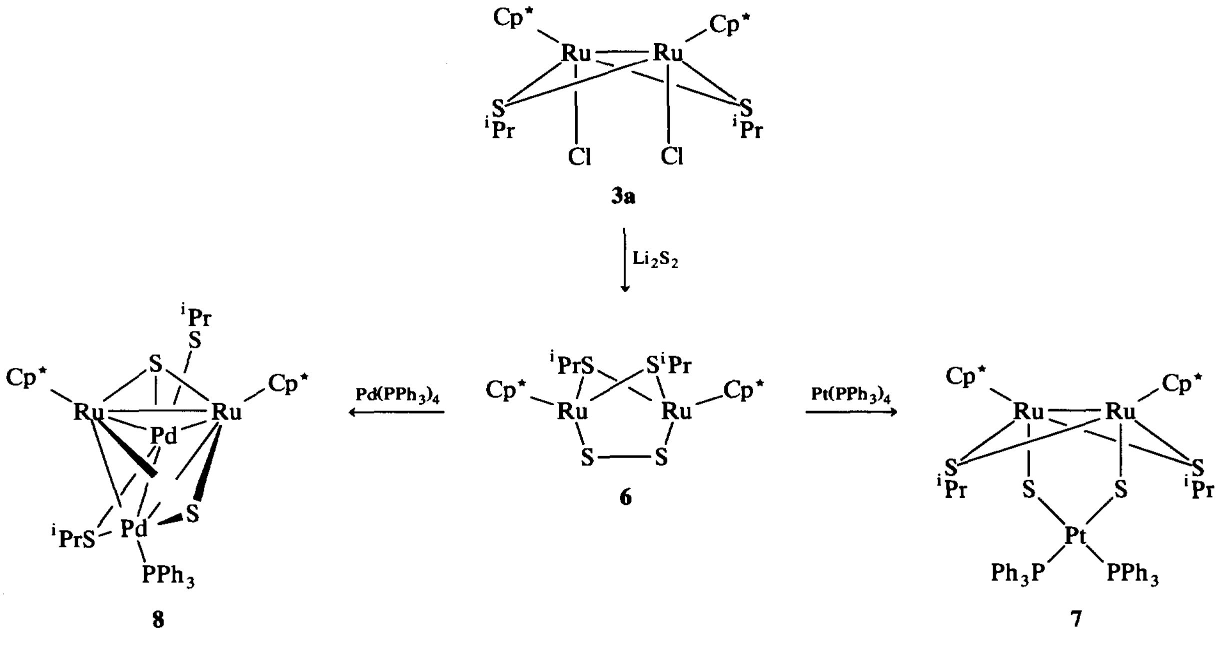
ence of Ru^{III} centres, complexes **2** and **3** are diamagnetic, which suggests the presence of a spin pairing between the two Ru centres (*vide infra*). On the other hand, in reactions with excess NaSR in MeOH at room temperature, **1** underwent replacement of the Cl ligands as well as the partial reduction of the Ru centre by the thiolates to give triply-bridged Ru^{II}/Ru^{III} complexes, $[Cp^*Ru(\mu_2\text{-}SR)_3RuCp^*]$ (**4**; R = alkyl, aryl) [18]. Concurrent formation of RSSR in almost the expected amount was confirmed in the run using NaSCy (Cy = cyclohexyl). Complexes **4** containing the formal Ru^{II}/Ru^{III} centre are paramagnetic and exhibit intense EPR signals both in solid and solution state. Furthermore, by the use of NaS^tBu, a doubly-bridged diamagnetic Ru^{II}/Ru^{II} complex, $[Cp^*Ru(\mu_2\text{-}S^tBu)_2RuCp^*]$ (**5b**), was obtained as the only isolable product. The more versatile method of synthesizing complexes of this class, $[Cp^*Ru(\mu_2\text{-}SR)_2RuCp^*]$ (**5**; R = alkyl, aryl), involves initial conversion of **1** into the Ru^{II} complex, either $[Cp^*Ru(\mu_2\text{-}OMe)_2RuCp^*]$ [19] or $[(Cp^*Ru)_4(\mu_3\text{-}Cl)_4]$ [14,20], followed by its reaction with $RSSiMe_3$ or NaSR, respectively (Scheme 2) [21].

3. Structures of thiolate-bridged diruthenium complexes

X-ray analyses have been undertaken to clarify the detailed structures of these new diruthenium complexes using single crystals of $[Cp^*Ru(\mu_2\text{-}SPh)_3RuCp^*]Cl$ (**2a**) [15,17], $[Cp^*Ru(\mu_2\text{-}S^iPr)_3RuCp^*]$ (**4a**) [18], and $[Cp^*Ru(\mu_2\text{-}SC_6H_3Me_2\text{-}2,6)_2RuCp^*]$ (**5c**) [21]. The structures of $[Cp^*RuCl(\mu_2\text{-}SR)_2Ru(Cl)Cp^*]$ [R = ^iPr (**3a**), Et] have also been determined by us quite recently; the details will be reported elsewhere.

In **2a**, there exists an Ru–Ru single bond surrounded by three symmetrically bridging SPh ligands between two Cp*Ru units [Ru–Ru distance: 2.630(1) Å]. The diamagnetic nature of **2** as described above is well explained by this spin pairing. Two mutually parallel Cp* ligands are in a staggered form and coordinate to the Ru atoms perpendicularly to the Ru–Ru vector. The structure of **4a** is quite analogous to that of **2a**, except that the Ru–Ru distance at 2.968(2) Å is significantly elongated from that in **2a**. That the coordination geometry around the metal is essentially similar for the two Ru atoms and the observed Ru–Ru bond order is less than unity suggest spin delocalization over the two Ru atoms.

The X-ray analysis of **5c** has unequivocally disclosed the absence of an Ru–Ru interaction in this complex [Ru–Ru distance: 3.500(2) Å]. Since the Ru–S distance at 2.350(4) Å is in the range of common Ru–S single bond lengths, **5c** apparently consists of the coordinatively unsaturated sixteen-electron Ru centres. In **5c**, the Ru_2S_2 ring is puckered with the dihedral angles of 131° and 139° along the Ru–Ru and S–S vectors, respectively, and two aryl groups are in a *syn* configuration with equatorial-equatorial disposition. Two mutually eclipsed Cp* ligands are slightly distorted to the



Scheme 3.

cis direction (dihedral angle: 15°). The X-ray structure of [Cp′Ru(μ_2-SEt)$_2$RuCp′] (Cp′ = η^5-C_5Me_4Et) reported independently by the other group is comparable to that of **5c** [22]. On the other hand, the variable-temperature NMR study of **5** has demonstrated the fluxional nature of these complexes in solutions ascribable to rapid Ru_2S_2 ring inversion.

The structure of **3** has also been demonstrated recently for the S^{i}Pr complex (**3a**) as well as the SEt complex. As expected from their diamagnetic nature, the Ru–Ru distances at 2.853(2) and 2.850(2) Å in these complexes, respectively, are consistent with the presence of an Ru–Ru single bond. Two Cp* ligands coordinated to the Ru atoms are mutually *cis* and two alkyl groups in the symmetrically bridging thiolate ligands exist in a *syn* form with axial-axial configuration.

4. Preparation of disulfide- and thiolate-bridged diruthenium complexes and mixed metal sulfide-thiolate clusters

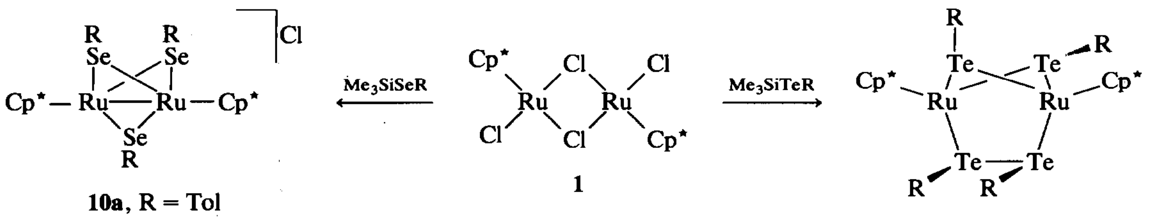
Upon treatment with Li_2S_2 in toluene at room temperature or excess $[NH_4]_2[MS_4]$ (M = W, Mo) in THF at reflux, **3a** afforded a diamagnetic disulfide- and thiolate-bridged diruthenium complex [Cp*Ru(μ_2-S_2)(μ_2-S^{i}Pr)$_2$RuCp*] (**6**) (Scheme 3) [23]. The structures of **6** and its SCH_2Ph analogue have been determined by X-ray crystallography. In **6**, two Ru atoms are symmetrically bridged by one $\eta^1:\eta^1$-S_2 ligand along with two S^{i}Pr ligands and two Ru atoms are separated by 3.590(2) Å, indicating the absence of any Ru–Ru interaction. The diamagnetic nature of **6** is therefore explained by S_2 ligand-based spin coupling, as observed earlier for the related Fe complex [CpFe(μ_2-S_2)(μ_2-SEt)$_2$FeCp] (Cp = η^5-C_5H_5) [24]. The particularly short Ru–S distances in the Ru–S–S–Ru moiety within **6** [2.209(5) and 2.215(4) Å] are diagnostic of this feature. Two ^{i}Pr groups are mutually *syn* with equatorial-equatorial configuration, while two Cp* ligands are distorted towards the direction opposite to the S_2 ligand, comprising the *cis* disposition. The structure of the SCH_2Ph analogue is essentially the same.

Interestingly, it has been demonstrated that **6** can serve as a versatile precursor to prepare novel mixed-metal sulfide-thiolate clusters (Scheme 3) [25]. Thus, treatment of **6** with $[Pt(PPh_3)_4]$ in toluene at 75°C afforded a trinuclear sulfide-thiolate cluster [$(Ph_3P)_2$Pt-(μ_2-S)$_2$(Cp*Ru)$_2$(μ_2-S^{i}Pr)$_2$] (**7**). X-ray analysis of **7** has shown the presence of an essentially planar five-membered core consisting of one Pt, two Ru and two S atoms, which results from the oxidative addition of the S_2 ligand in **6** to a zero-valent Pt atom and concurrent Ru–Ru bond formation. Two Ru atoms are further connected by two S^{i}Pr bridges.

In contrast, the Pd complex $[Pd(PPh_3)_4]$ is less reactive than its Pt analogue but does react under more forcing conditions to give a tetranuclear cluster [$Pd_2(PPh_3)$(S^{i}Pr)(μ_2-S^{i}Pr)(μ^3-S)$_2$(Cp*Ru)$_2$] (**8**). In **8**, two Pd and two Ru atoms form a distorted tetrahedron, in which the Pd–Pd and Ru–Ru distances at 2.803(2) and 2.628(3) Å feature metal–metal single bonds, whereas the relatively long Pd–Ru distances (2.86–3.10 Å) suggest the weaker Pd–Ru interaction. Two $PdRu_2$ faces are capped by the μ_3-S ligand resulting from the S–S bond cleavage of the S_2 ligand in **6**. Both S^{i}Pr ligands originally attached to the Ru atoms migrate to the Pd atoms.

5. Preparation of selenolate- and tellurolate-bridged diruthenium complexes

Complex **1** is an excellent precursor not only of diruthenium-thiolate compounds but also of diruthenium-tellurolate and -selenolate complexes. Thus, reactions of **1** with Me_3SiTeR (R = Tol, Ph; Tol = *p*-tolyl) produced diarylditelluride- and aryltellurolate-bridged Ru^{II}/Ru^{II} complexes [Cp*Ru(μ_2-RTeTeR)(μ_2-TeR)$_2$-RuCp*] (**9**), whereas those with Me_3SiSeR (R = Tol, Ph) yielded arylselenolate-bridged Ru^{III}/Ru^{III} complexes [Cp*Ru(μ_2-SeR)$_3$RuCp*]Cl (**10**) (Scheme 4)



10a, R = Tol
10b, R = Ph

1

9a, R = Tol
9b, R = Ph

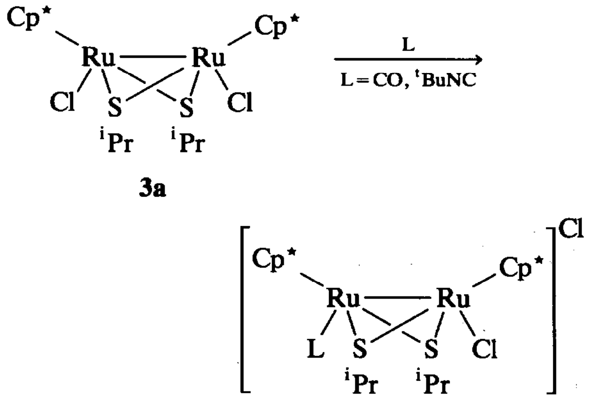
Scheme 4.

[26]. Complexes **9a** (R = Tol) and **10a** (R = Tol) have been fully defined by X-ray crystallography.

Of great interest is that the RTeTeR bridges the two Ru atoms which is formed presumably by coupling of two TeR ligands at the diruthenium site [Te–Te distance: 2.901(3) Å]. Diorganoditellurides most commonly undergo cleavage of their Te–Te bond with formal oxidation of the metal centre to form terminal or bridging tellurolate ligands [27]. The only well-characterized intact coordinated diorganoditelluride complex is $[(CO)_3Re(\mu_2\text{-PhTeTePh})(\mu_2\text{-Br})_2Re(CO)_3]$ [Te–Te bond distance: 2.794(5) Å] obtained by displacement of THF in $[(CO)_3(THF)Re(\mu_2\text{-Br})]_2$ by PhTeTePh [28]. Complexes **9** are considered to be formed by dinuclear reductive coupling of two tellurolate ligands at the diruthenium site. The Ru–Ru distance of 4.052(3) Å, which is significantly longer than the values observed in diruthenium complexes having a Ru–Ru single bond described above, clearly indicates the absence of bonding interaction between the two Ru atoms. On the other hand, the structural features of **10a** are essentially similar to those of the related thiolate-bridged complex **2a**.

6. Reactions of diruthenium complexes with CO, ^{t}BuNC, H_2 and alkyl halides

Treatment of **3a** with CO in CH_2Cl_2 at room temperature and ^{t}BuNC in THF at reflux resulted in the formation of cationic complexes $[Cp^*Ru(Cl)(\mu_2\text{-}S^iPr)_2Ru(L)Cp^*]Cl$ (L = CO, ^{t}BuNC) (eqn. 1) [17]. Facile coordination of such a π-acidic molecule like CO on the Ru^{III} centre in **3a** may be explained by the significant electron donating ability of the S^iPr ligands.



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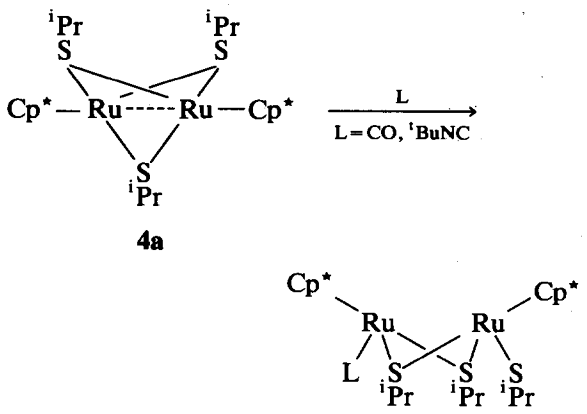

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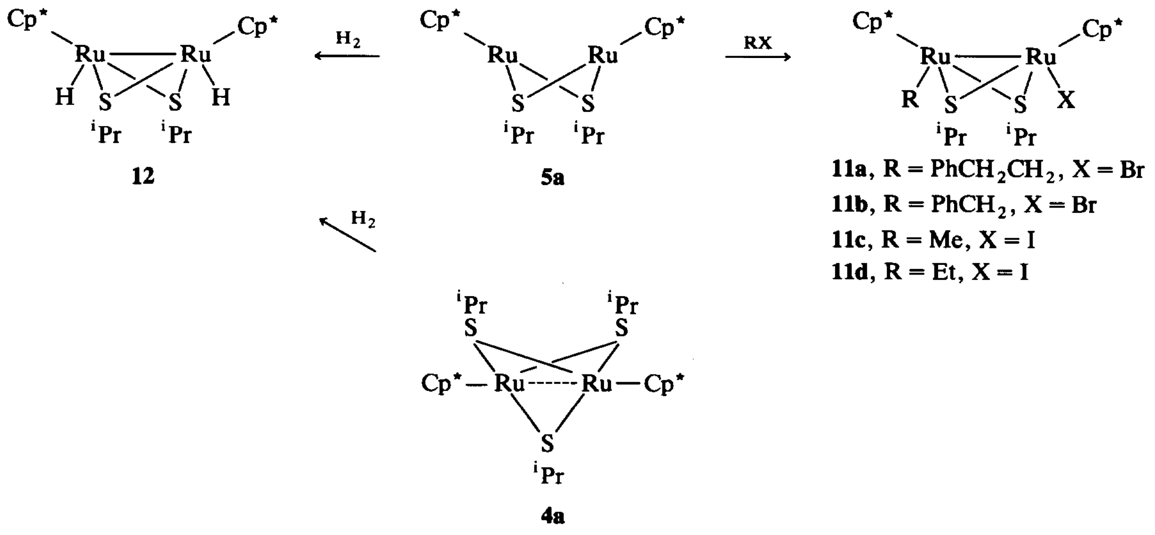
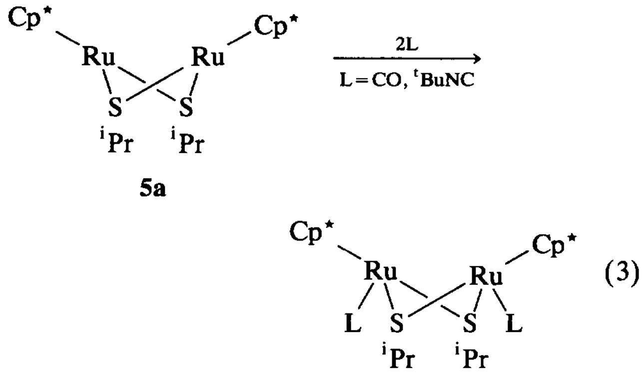


11a, R = $PhCH_2CH_2$, X = Br
11b, R = $PhCH_2$, X = Br
11c, R = Me, X = I
11d, R = Et, X = I

Scheme 5.

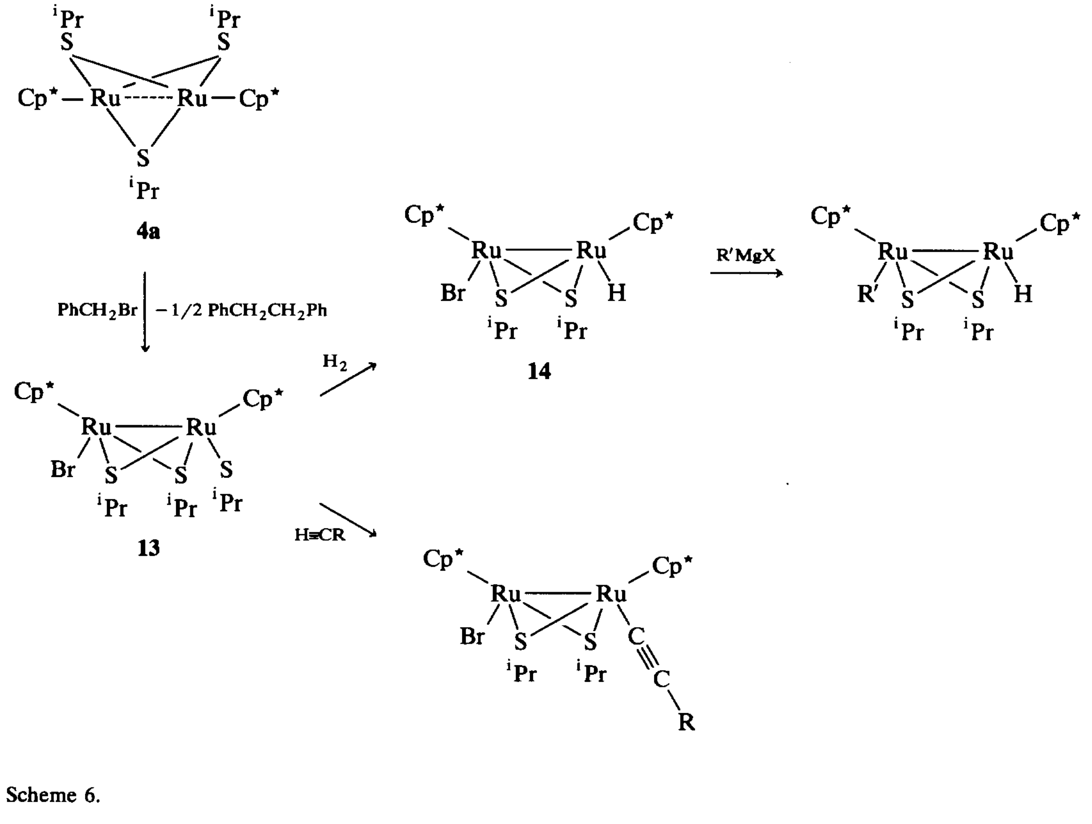


Reactions of **4a** and **5a** with CO and ^{t}BuNC also took place both at room temperature, affording [Cp*Ru(L)(μ_2-S^{i}Pr)$_2$Ru(S^{i}Pr)Cp*] and [Cp*Ru(L)(μ_2-S^{i}Pr)$_2$Ru(L)Cp*], respectively (eqns. 2 and 3) [18].

In addition to the simple coordination of substrate molecules, diruthenium complexes containing Ru^{II} centre(s), **5a** and **4a**, exhibit intriguing reactivities toward alkyl halides and H_2. Thus, **5a** reacted rapidly with a series of alkyl bromides and iodides (RX) in hexane at room temperature to give diruthenium complexes [Cp*Ru(R)(μ_2-S^{i}Pr)$_2$Ru(X)Cp*] (**11**) (Scheme 5) [21]. The structure of these products resulting from the dinuclear oxidative addition of RX across the coordinatively unsaturated diruthenium centre has been unambiguously demonstrated for **11a** (R = $PhCH_2CH_2$, X = Br). The important structural features in **11a** are comparable to those in **3**, which include the presence of a Ru–Ru single bond [Ru–Ru distance: 2.844(1) Å], mutually *cis* configuration of two Cp* ligands, and a *syn* orientation of two ^{i}Pr groups with axial-axial disposition. Following study on the reactivities of **11** has recently demonstrated that several alkyl-alkyl and alkyl-alkynyl complexes can be obtained by treatment of **11** with R′MgX or R′Li, the details of which will be reported subsequently.

Dinuclear oxidative addition of H_2 towards **5a** also occurred at room temperature, affording the corresponding dihydrido complex [Cp*Ru(H)(μ_2-S^{i}Pr)$_2$Ru(H)Cp*] (**12**) [21]. Although we could not locate the hydrido ligands due to the poor quality of the diffraction data, the connecting scheme of non-hydrogen atoms within **12** appears to be analogous to that in **3** and **11a**, suggesting the presence of two terminal hydride ligands on each Ru atom. [18]

Formation of **11** and of **12** from **5a** give interesting examples of addition of alkyl halides and H_2 to the multi-metallic sites, although the detailed mechanism of the reactions reported here are still uncertain. The related addition of molecular H_2 to dinuclear centres bridged by two thiolate ligands has been observed for the Ir complex [Ir(CO){P(OMe)$_3$}(μ_2-S^{t}Bu)$_2$Ir(CO){P(OMe)$_3$}], affording [Ir(H)(CO){P(OMe)$_3$}(μ_2-

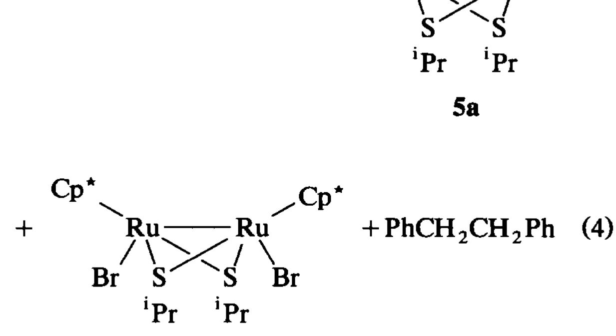


Scheme 6.

S^{t}Bu)$_2$Ir(H)(CO){P(OMe)$_3$}] [29]. The MO study of H$_2$ addition to d^8/d^8 metal centres (Ir/Ir or Rh/Rh) [30] as well as some experimental evidence suggest a two step mechanism involving initial addition of H$_2$ to a single metal and successive migration of one hydride to the other metal [31]. Isolation of [Rh(COMe)(I)(PMe$_2$Ph)(μ_2-S^{t}Bu)$_2$Rh(CO)(PMe$_2$Ph)] from the reaction of [Rh(CO)(PMe$_2$Ph)(μ_2-S^{t}Bu)$_2$Rh(CO)(PMe$_2$Ph)] with MeI may also indicate that the oxidative addition first occurs on a single metal centre in this reaction [32].

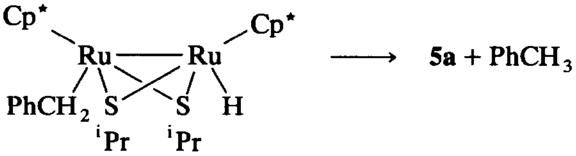
Complex **4a** also reacted with H$_2$ to give **12** in moderate yield [18]. On the other hand, reaction of **4a** with PhCH$_2$Br afforded [Cp*Ru(Br)(μ_2-S^{i}Pr)$_2$Ru(S^{i}Pr)Cp*] (**13**) and PhCH$_2$CH$_2$Ph (Scheme 6). From **13** was derived a series of diruthenium complexes [Cp*Ru(Br)(μ_2-S^{i}Pr)$_2$Ru(R)Cp*] [R = H (**14**), alkynyl] upon treatment with H$_2$ gas or terminal alkynes. Complex **14** proved to be further converted to the alkyl-hydrido complexes [Cp*Ru(R′)(μ_2-S^{i}Pr)$_2$Ru(H)Cp*] by reaction with R′MgX [33].

Interestingly, among the various diruthenium thiolate complexes containing σ-alkyl ligands obtained here, only the benzyl complexes [Cp*Ru(CH$_2$Ph)(μ_2-S^{i}Pr)$_2$Ru(Br)Cp*] and [Cp*Ru(CH$_2$Ph)(μ_2-S^{i}Pr)$_2$Ru(H)Cp*] are specifically unstable. Both decompose readily at room temperature and the former produces a mixture of [Cp*Ru(μ_2-S^{i}Pr)$_2$RuCp*] (**5a**), [Cp*Ru(Br)(μ_2-S^{i}Pr)$_2$Ru(Br)Cp*], and PhCH$_2$CH$_2$Ph (eqn. 4), the latter giving **5a** and PhCH$_3$ (eqn. 5). The latter reaction is especially noteworthy as one of the still rare examples of a well-defined dinuclear reductive elimination reaction. In contrast, the benzyl-methyl complex [Cp*Ru(CH$_2$Ph)(μ_2-S^{i}Pr)$_2$Ru(Me)Cp*] is quite robust under analogous conditions.



5a

(4)



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7. Reactions with terminal alkynes

The dinuclear ruthenium thiolate complexes **4a**, **5a** and [Cp*Ru(μ_2-Cl)(μ_2-S^{i}Pr)$_2$RuCp*][OTf] (OTf = OSO$_2$CF$_3$) derived from **3a**, readily reacted with various terminal alkynes to form a variety of novel diruthenium complexes. These reactions were surprisingly sensitive to the nature of the diruthenium centre and the alkyne substituents. Among the dinuclear complexes described below, the following have been fully characterized by X-ray crystallography: **15–18**, **19a**, **22a**, **23a**, **27a**, **28**, **32** and **33a**.

7.1. Reactions of 5a with terminal alkynes (Scheme 7)

Complex **5a** reacted with HC≡CSiMe$_3$ to yield a bridging alkyne complex **15**, in which two Ru atoms are bridged by the η^2-μ_2-Me$_3$SiC≡CC(=CHSiMe$_3$)C≡CSiMe$_3$ moiety formed by oxidative trimerization of HC≡CSiMe$_3$ on the diruthenium site in a branched and acyclic manner [34]. The free alkyne trimer (Me$_3$SiC≡C)$_2$C=CHSiMe$_3$ can be easily released from **15** by air oxidation in almost quantitative yield. Recently Tilley reported that treatment of [(Cp*Ru)$_4$(μ_3-Cl)$_4$] with HC≡CSiMe$_3$ yielded a triruthenium cluster [Cp$^*_3$Ru$_3$(μ_2-Cl)$_2$(μ_3-Cl)(η^2-μ_2-HC≡CSiMe$_3$)] (with 1 equiv of HC≡CSiMe$_3$) or a mixture of a cyclobutadiene complex Cp*Ru[η^4-C$_4$H$_2$(SiMe$_3$)$_2$]Cl and a ruthenacyclopentadiene complex [Cp*RuCl$_2${η^2 : η^4-μ_2-C$_4$H$_2$(SiMe$_3$)$_2$}RuCp*] (with excess HC≡CSiMe$_3$) [35]. It is noteworthy that completely different products are formed depending upon the types of Cp*Ru^{II} species.

In contrast, reaction of **5a** with HC≡CTol gave a dinuclear ruthenacyclopentenyl complex **16**, in which three HC≡CTol molecules are incorporated into the diruthenium centre accompanied by ring closure [36]. The two alkyne molecules form a five-membered metallacycle with one Ru atom, a part of which is bound to another Ru atom via π-allyl type coordination. To the best of our knowledge, this is the first example of any transformation in which alkynes are converted to form the metallacycle having such a specific structure. Another interesting point to note is formal insertion of the alkyne molecules into the Ru–S bond in **5a**. Although several mono- and dinuclear thiolate compounds have been reported to undergo insertion of alkynes into the metal–sulfur bond, these reactions have been strictly limited to those with fluorinated alkynes, *e.g.*, CF$_3$≡CF$_3$ [37].

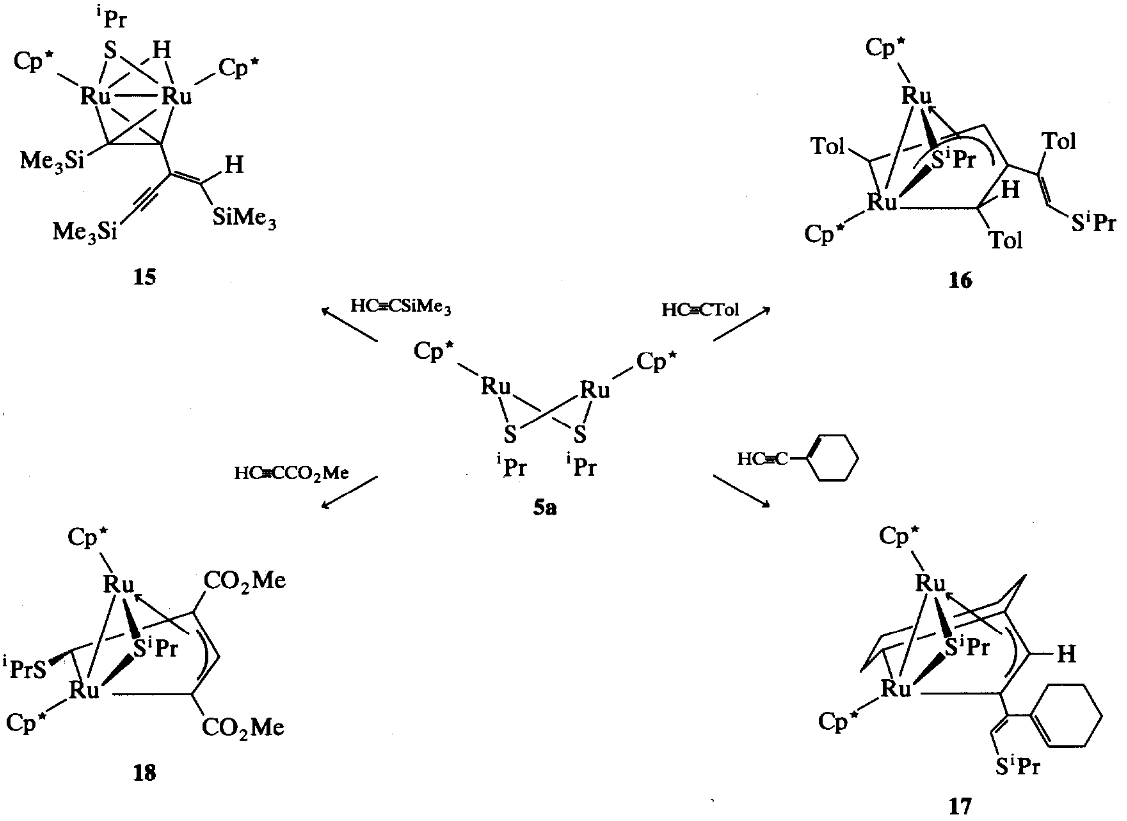
Treatment of **5a** with $HC{\equiv}C\overline{C{=}CH(CH_2)_3C}H_2$ yielded another type of dinuclear ruthenacyclopentenyl complex **17** [36]. In this case, the two alkyne molecules are incorporated into the diruthenium site in **5a**. The five-membered metallacycle in **17** is formed by the conjugated enyne unit in one alkyne molecule and one of the Ru atoms, apparently owing to the presence of the original C=C bond at a suitable position for ring closure.

Reaction of **5a** with $HC{\equiv}CCO_2Me$ also proceeded smoothly to give the related dinuclear ruthenacyclopentenyl complex **18**, in which consecutive insertion of the two alkyne molecules into the Ru–S bond results in the formation of the metallacycle framework. Mechanistic investigation on these transformations of alkynes at the coordinatively unsaturated diruthenium site in **5a** will be reported in due course.

7.2. *Reactions of [Cp*Ru(μ_2-S^{i}Pr)$_3$RuCp*]* **4a** *with terminal alkynes*

Paramagnetic complex Cp*Ru(μ_2-S^{i}Pr)$_3$RuCp* (**4a**) reacted with terminal alkynes HC≡CR [R = Tol, Ph, $\overline{C{=}CH(CH_2)_3C}H_2$] at room temperature to give the dinuclear terminal dialkynyl complexes [Cp*Ru(C≡CR)(μ_2-S^{i}Pr)$_2$Ru(C≡CR)Cp*] (**19**) (Scheme 8) [38]. Two alkynyl ligands are on adjacent Ru atoms and take a mutually *cis* configuration. Similar treatment of **4a** with HC≡C^{t}Bu afforded the dinuclear monoalkynyl complex [Cp*Ru(C≡C^{t}Bu)(μ_2-S^{i}Pr)$_2$Ru(S^{i}Pr)Cp*] (**20**), which further reacted with terminal alkynes at 90°C to form the (mixed) dialkynyl complexes [Cp*Ru(C≡C^{t}Bu)(μ_2-S^{i}Pr)$_2$Ru(C≡CR)Cp*] (**21**) [38]. Although a large number of metal clusters containing alkynyl ligands are known, polynuclear complexes with terminal alkynyl ligands are remarkably rare [39]. This is probably due to the ease with which the C≡C bond can interact with the other metals in the cluster framework.

Mononuclear η^1-alkynyl complexes are well known to react with electrophiles at the β-carbon to form stable vinylidene complexes, which can be further converted to compounds with a variety of η^1-carbon-bonded ligands such as vinyl ethers, carbenes, acyls and alkyls [40]. In a study on the reactivities of the terminal alkynyl ligands on the thiolate-bridged diruthenium centre in **19**, we have investigated reactions of **19** with HBF_4 or I_2. Unexpectedly, these reactions did not yield the corresponding dinuclear vinylidene complexes but instead resulted in an unprecedented series of



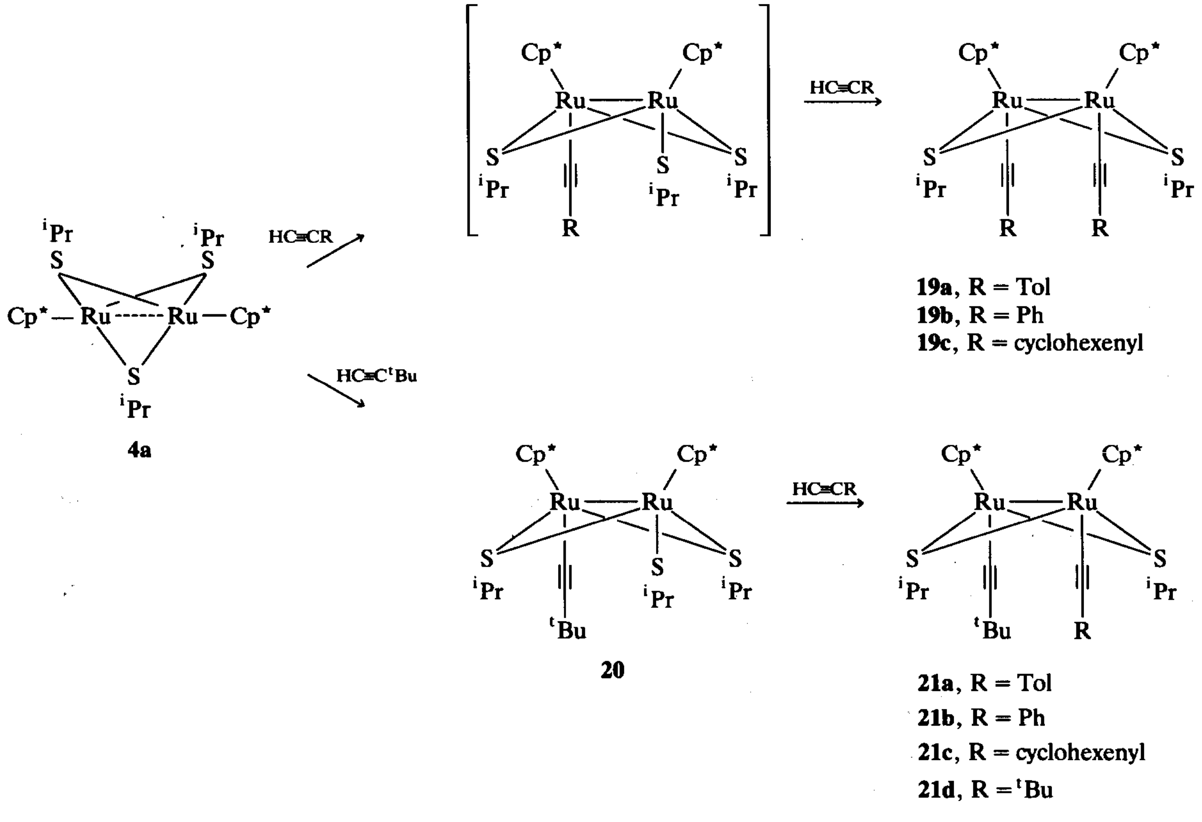
Scheme 7.

transformations. Complexes **19a** (R = Tol) and **19b** (R = Ph) readily reacted with HBF_4 to give the diruthenacyclopentadienoindane complexes **22a** (R′ = Me) and **22b** (R′ = H) respectively in excellent yields, which are formed by unique coupling of two terminal alkynyl ligands on the thiolate-bridged diruthenium centre (Scheme 9) [38]. Quantitative deprotonation reactions of **22** with base proceed smoothly to give the diruthenacyclopentenoindene complexes **23**, which react with HBF_4 to reproduce **22**. Since complexes **19a** and **19b** are readily available from **4a** and alkynes, the present reactions offer a potential route to substituted indane and indene derivatives from terminal alkynes.

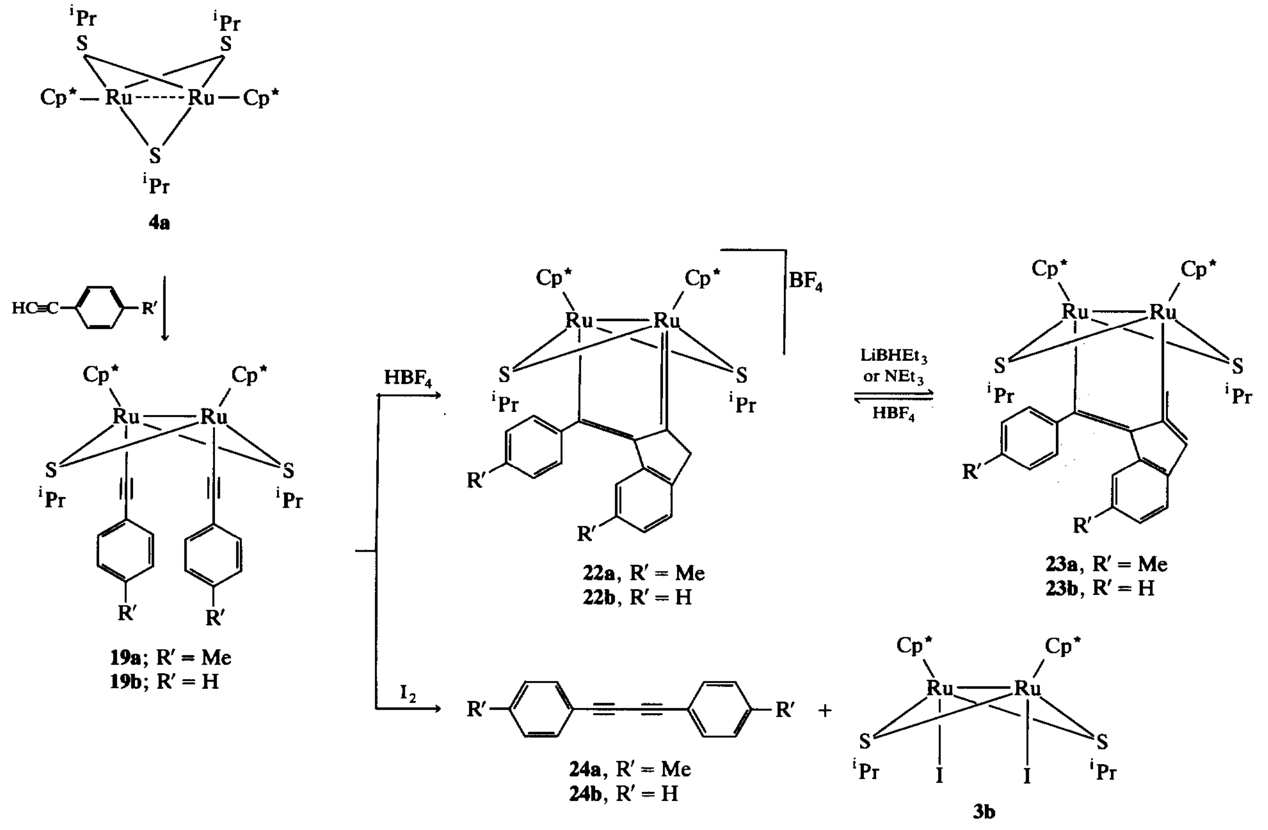
The mechanism proposed for the formation of **22** is shown in Scheme 10. The initial step is the proton addition to a C_β of one of the two terminal alkynyl ligands to give a dinuclear alkynyl-vinylidene intermediate **25**. The next step would involve alkynyl migration to the vinylidene ligand in **25** to give a dinuclear η^1-butenynyl intermediate **26**. Recently Wakatsuki *et al.* reported intramolecular migration of an alkynyl to a vinylidene ligand on a mononuclear ruthenium centre to form the η^1-butenynyl complex $[RuCl(CO)(PPh_3)_2\{C(C{\equiv}C^tBu){=}CH^tBu\}]$ [41]. The C≡C moiety bonded to the cationic Ru^{III} centre in the intermediate **26** could undergo intramolecular nucleophilic attack by the aromatic group to form the initial product **23**. Evidence for the formation of **23** prior to **22** comes from the finding that treatment of **19a** with a catalytic amount of HBF_4 (0.1 equiv) affords **23a** in 40% yield. Complex **23** would then be protonated to give the final product **22**.

When I_2 was used as an electrophile, another type of reaction occurred. Addition of I_2 to a THF solution of **19a** or **19b** induced liberation of 1,4-disubstituted-1,3-diynes **24** from the diruthenium site in good yield, concurrent with formation of complex **3b** (Scheme 9) [38]. Halogens are known to add to the C_β in several alkynyl ligands to form the corresponding vinylidenes. Bruce and co-workers reported that reactions of halogens with $[Cp(PPh_3)_2Ru(C{\equiv}CPh)]$ afforded a halovinylidene complex $[Cp(PPh_3)_2Ru({=}C{=}CXPh)]X_3$ (X = Cl, Br, I); in some cases halogenation of the phenyl group of the C≡CPh ligand also occurred to give $[Cp(PPh_3)_2Ru\{{=}C{=}CBr(C_6H_4Br\text{-}p)\}]Br_3$ [42]. These reactions demonstrate the remarkable resistance of the Ru–C(sp) bond toward cleavage by halogens. In sharp contrast, the Ru–C(sp) bonds in **19a** and **19b** were so smoothly and cleanly cleaved by I_2 to give the 1,4-disubstituted-1,3-butadiynes.

The formal dinuclear reductive elimination induced by I_2 described above is particularly interesting because it is believed that the intramolecular dinuclear



Scheme 8.



Scheme 9.

reductive elimination: $L_4(R)M{-}M(R)L_4 \rightarrow R_2 + L_4M{=}ML_4$ (R = H, Me) is symmetry forbidden and exhibits a large activation energy for a C_{2v} concerted least-motion pathway [43]. Actually, Chisholm and co-workers previously observed that complex $(Me_2N)_2Mo(Et){\equiv}Mo(Et)(NMe_2)_2$ does not give butane when treated with CO_2 or alcohol, but yields ethylene and ethane [44].

Interestingly, propargyl alcohols reacted with **4a** in quite a different manner. Corresponding dialkynyl complexes were not produced upon treatment of **4a** with $HC{\equiv}CC(OH)R_2$ (R = Ph, Tol, Me), but instead unusual coupling of the propargyl alcohols on the diruthenium site proceeded to yield new types of dinuclear metallacycles **27** and **28** (Scheme 11) [45]. Complexes **27** have the diruthenacyclopentanone unit with both diarylmethylene and diarylvinylidene substituents, produced by coupling of the two alkyne molecules on the diruthenium site in **4a** accompanied by pseudo 1,3-shift of an oxygen atom. To the best of our knowledge, this is the first example of any transformation in which propargyl alcohols are converted in such a manner on metal centres. Similar treatment of **4a** with $HC{\equiv}CC(OH)Me_2$ did not give the methyl analogue of **27** but yielded a diruthenacyclopentenone complex **28**, indicating that another type of coupling of propargyl alcohol has proceeded to form the fused ring system.

One possible pathway for the formation of **27** and **28** could involve intramolecular C–C bond formation between either alkynyl and allenylidene or alkynyl and vinylvinylidene ligands in intermediates **29** and **30**, respectively [46*], although we must await further investigation to elucidate the detailed reaction mechanisms. Compared with the coupling of two terminal alkynyl ligands ($-C{\equiv}CAr$) at the diruthenium centre described above, the present reaction offers a related but quite

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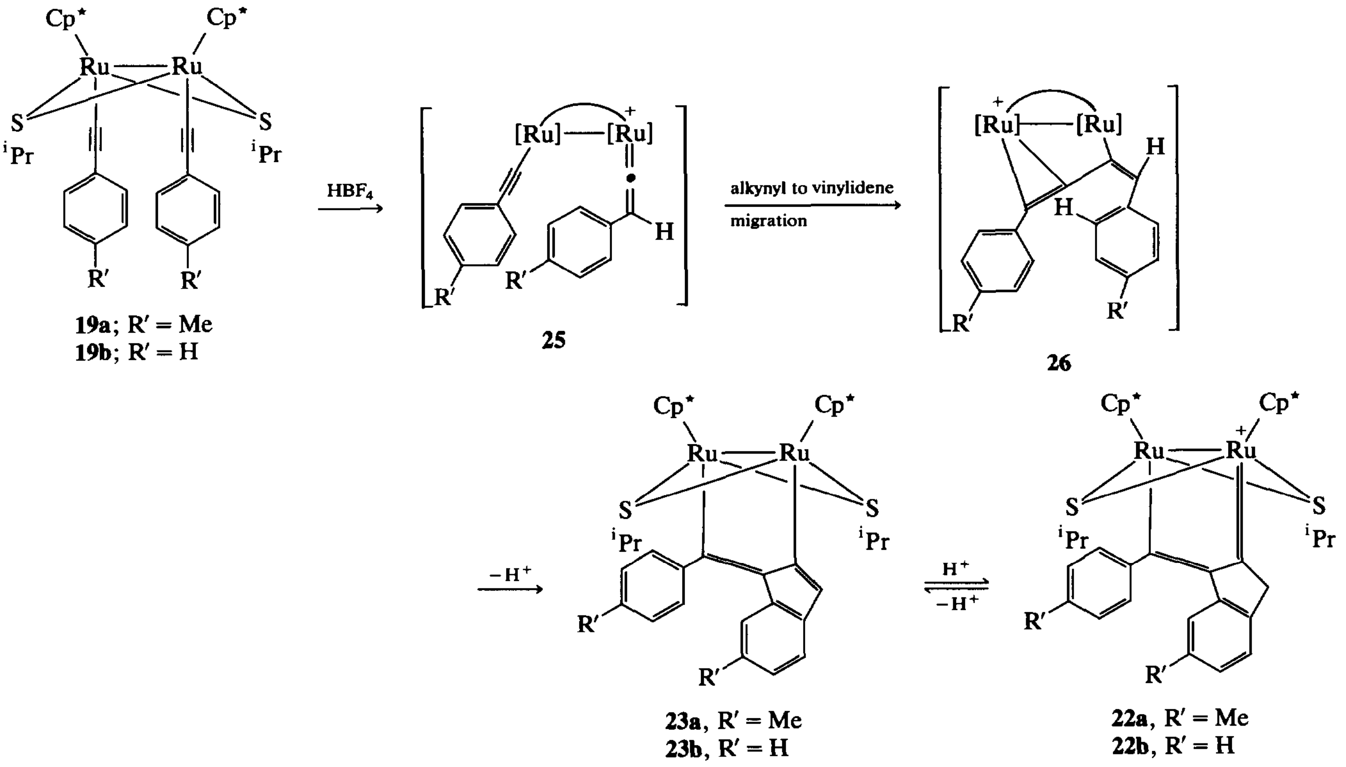
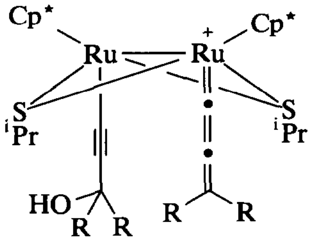
* Reference number with an asterisk indicate a note in the list of references.

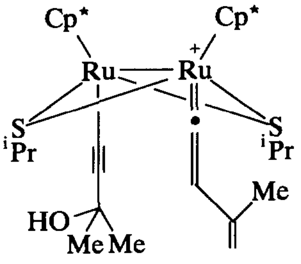


Scheme 10.

different type of activation and transformation of alkynes on the thiolate-bridged diruthenium template.



29
R = Tol, Ph

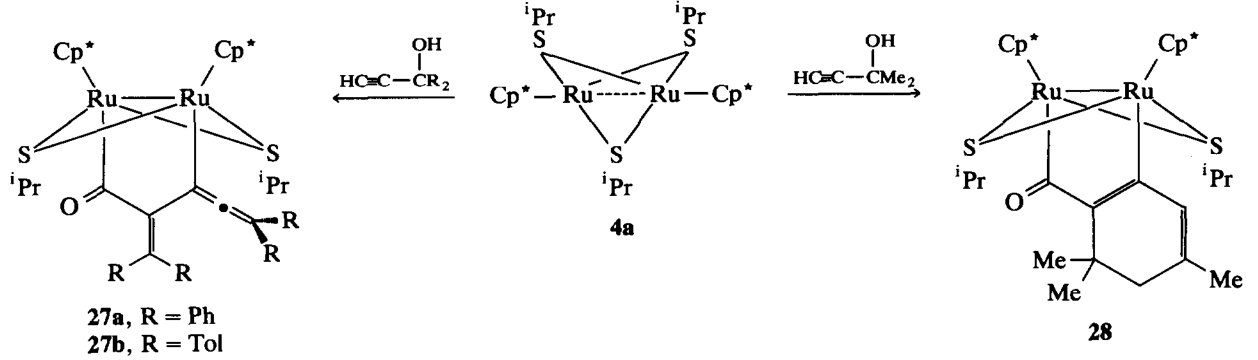


30

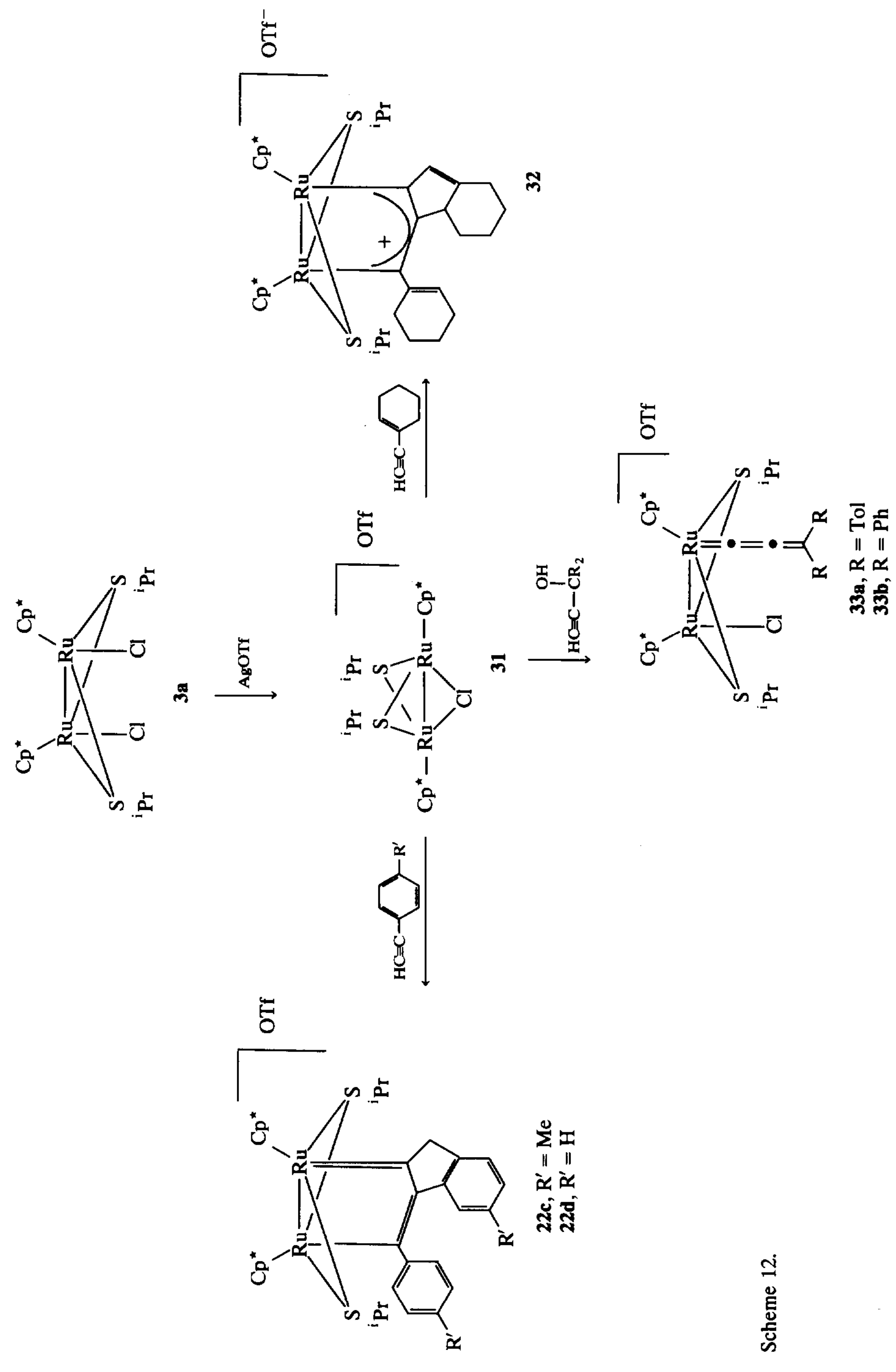
We believe this kind of work lays the foundation for future investigation into developing the vinylidene-alkynyl, allenylidene-alkynyl and vinylvinylidene-alkynyl couplings on the bimetallic centre into synthetically useful reactions.

7.3. Reactions of $[Cp^*Ru(\mu_2\text{-}Cl)(\mu_2\text{-}S^iPr)_2RuCp^*][OTf]$ *(31)* $(OTf = OSO_2CF_3)$ *with terminal alkynes (Scheme 12)*

Although $[Cp^*Ru(Cl)(\mu_2\text{-}S^iPr)_2Ru(Cl)Cp^*]$ (**3a**) did not itself react with alkynes in THF, addition of AgOTf to **3a** formed a highly reactive cationic complex

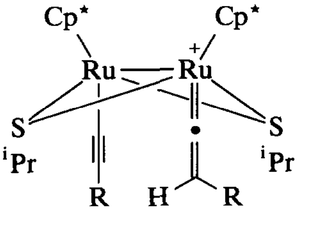


Scheme 11.


Cp*
Ru
S
ⁱPr
Cl
3a
AgOTf
31
OTf
OTf⁻
HC≡C—
HC≡C—CR₂
OH
32
+
R'
22c, R' = Me
22d, R' = H
R
33a, R = Tol
33b, R = Ph

Scheme 12.

$[Cp^*Ru(\mu_2\text{-}Cl)(\mu_2\text{-}S^iPr)_2RuCp^*][OTf]$ (**31**), which readily incorporated alkynes. Thus, treatment of **31** with $HC{\equiv}CR$ (R = Tol, Ph) afforded diruthenacyclopentadienoindane complexes **22c** and **22d** (Scheme 12) [47]. Similar complexes **22a** and **22b** were alternatively obtained by protonation of dialkynyl complexes $[Cp^*Ru(C{\equiv}CR)(\mu_2\text{-}S^iPr)_2Ru(C{\equiv}CR)Cp^*]$ (**19a**, R = Tol; **19b**, R = Ph) (*vide surpra*) [38]. It is interesting to note that $HC{\equiv}CR$ (R = Tol, Ph) directly coupled on the diruthenium site to produce **22c** and **22d** in high yields. Similar high reactivity of **31** towards $HC{\equiv}C\overline{C{=}CH(CH_2)_3CH_2}$ has also been demonstrated by instant formation of **32**, which could not be obtained by protonation of a corresponding dialkynyl complex **19c** (R = $\overline{C{=}CH(CH_2)_3CH_2}$) [38]. The unique chemical transformation of these terminal alkynes at the diruthenium centre to afford complexes **22c**, **22d** and **32** is considered to proceed via vinylidene-alkynyl intermediates like **34**, which were proposed for the coupling of two terminal alkynyl moieties in **19** [38]. In contrast, complex **31** reacted with $HC{\equiv}CC(OH)R_2$ (R = Tol, Ph) to give dinuclear terminal allenylidene complexes **33**. Finally, it should be mentioned that the transformations of alkynes described here proceed without isolating the cationic complex **31**. Thus, addition of the corresponding alkynes to a mixture of **3a** and AgOTf in THF results in the clean formation of **22c**, **22d**, **32** and **33**.



34

R = Tol, Ph, cyclohexenyl

8. Conclusion

The present study has given entry into an impressive array of dinuclear ruthenium thiolate complexes. A variety of novel chemical transformations has been performed at the well-defined thiolate bridged diruthenium centre, which have not been realized at the monometallic centre. The chemistry of ruthenium thiolate complexes has also been extended to preparation of mixed-metal sulfide clusters and diruthenium tellurium and selenium complexes. Further studies are in progress aimed at synthesizing polynuclear transition metal-sulfur, -selenium, and -tellurium complexes which provide the well-defined multimetallic centres for unique and efficient transformations of organic substrates.

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