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Stepwise Syntheses of a Series of Thiolate-Bridged Diruthenium Complexes [Cp*RuBr(μ-SPr^i)$_2$RuCp*X] (Cp* = η^5-C_5Me_5; X = SPr^i, alkynyl, H) and [Cp*RuR(μ-SPr^i)$_2$RuCp*H] (R = CH_2Ph, CH_2CH_2Ph). Facile Dinuclear Reductive Elimination of $PhCH_3$ from [Cp*Ru(CH_2Ph)(μ-SPr^i)$_2$RuCp*H]

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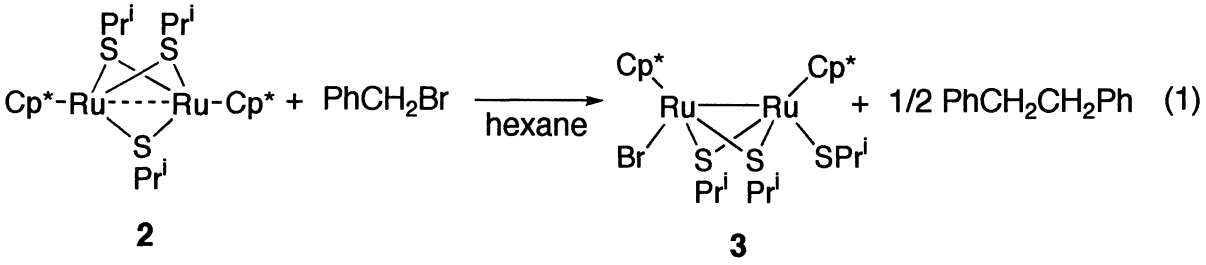
Diruthenium complex [Cp*Ru(μ-SPr^i)$_3$RuCp*] (Cp* = η^5-C_5Me_5) reacted with $PhCH_2Br$ to give [Cp*RuBr(μ-SPr^i)$_2$RuCp*(SPr^i)] (**3**) and $PhCH_2CH_2Ph$. Treatment of **3** with HC≡CR (R = Bu^t, 4-MeC_6H_4) or H_2 resulted in the formation of [Cp*RuBr(μ-SPr^i)$_2$RuCp*(C≡CR)] (**4**) or [Cp*RuBr(μ-SPr^i)$_2$RuCp*H] (**5**), respectively. Complex **5** was further converted into [Cp*RuR(μ-SPr^i)$_2$RuCp*H] (**6a**: R = $PhCH_2$; **6b**: R = $PhCH_2CH_2$) by the reaction with RMgX (X = Cl, Br). In contrast to the inertness of **6b**, **6a** dissolved in benzene underwent dinuclear reductuve elimenation to give PhMe in high yield at room temperature, accompanied by the generation of [Cp*Ru(μ-SPr^i)$_2$RuCp*].

Recent research in this laboratory has shown that a series of diruthenium complexes containing Ru(II) and/or Ru(III) centers bridged by two or three thiolate ligands can be prepared from the reactions of [Cp*RuCl(μ-Cl)$_2$RuCp*Cl] and various thiolate compounds.[1)] Among the four types of diruthenium complexes isolated to date, the diamagnetic Ru(II)/Ru(II) complex [Cp*Ru(μ-SPr^i)$_2$RuCp*] (**1**) and the paramagnetic Ru(II)/Ru(III) complex [Cp*Ru(μ-SPr^i)$_3$RuCp*] (**2**) are of particular importance, since these complexes display unique reactivities towards substrates such as alkynes, H_2, CO, and isocyanides.[1b-d, 2)] The reactions of **1** with alkyl halides have also been investigated and as reported in a preceeding paper the alkyl-halido complexes [Cp*RuR(μ-SPr^i)$_2$RuCp*X] have been obtained by the dinuclear oxidative addition of RX across the diruthenium center in **1**.[1d)] Now we have found that the reaction of **2** with $PhCH_2Br$ gives a new bromo-thiolato complex [Cp*RuBr(μ-SPr^i)$_2$RuCp*(SPr^i)] (**3**), from which a significant body of new diruthenium complexes can be derived. We wish to describe herein the details of these new diruthenium complexes.

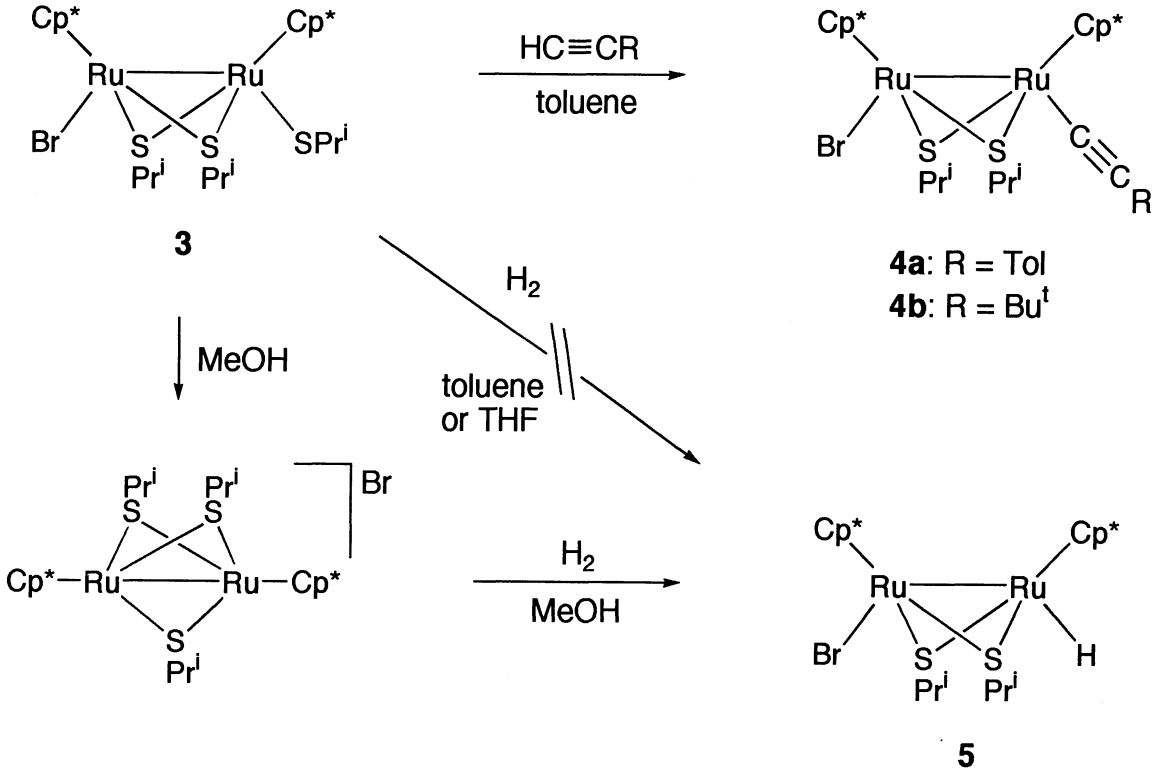
Treatment of **2** with an equimolar amount of $PhCH_2Br$ afforded the diamagnetic diruthenium complex **3**, which was isolated as a pale brown solid in 58% yield.[3)] The GLC analysis of the reaction mixture disclosed the concurrent formation of $PhCH_2CH_2Ph$ in 80% yield based on the stoichiometry shown in eq 1. The ^1H NMR data of **3** are in good agreement with those of the previously reported dinuclear Ru(III) complexes containing two inequivalent Ru centers connected by two bridging SPr^i ligands as well as a Ru-Ru single bond.[1, 2b)]

Complex **3** dissolved in toluene reacted with either HC≡CTol (Tol = 4-MeC_6H_4) at reflux or HC≡CBu^t at 50 °C to give dinuclear alkynyl complexes [Cp*RuBr(μ-SPr^i)$_2$RuCp*(C≡CR)] (**4**) as dark brown solids in



58 and 28% yields for R = Tol (**4a**) and R = Bu^t (**4b**), respectively (Scheme 1).[4] Presence of the terminal alkynyl ligands in **4** has been unambiguously manifested by their IR spectra (KBr disk), exhibiting the characteristic ν(C≡C) bands at 2091 (**4a**) and 2110 cm^{-1} (**4b**), which are comparable to those of the relating diruthenium complexes such as [Cp*Ru(C≡CTol)(μ-SPr^i)$_2$RuCp*(C≡CTol)] (2100 cm^{-1}) and [Cp*Ru-(SPr^i)(μ-SPr^i)$_2$RuCp*(C≡CBu^t)] (2099 cm^{-1}).[2b] The ^{1}H NMR spectra are also consistent with the structure shown in Scheme 1.

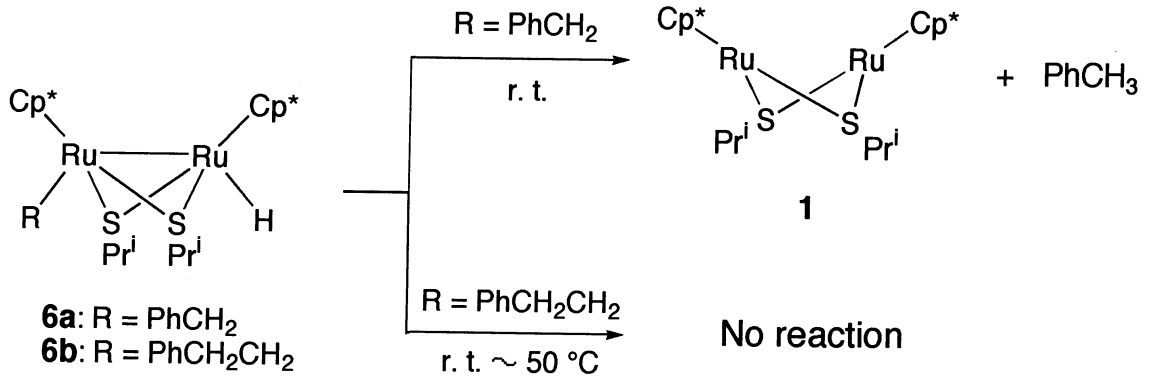
The reaction of **3** with H_2 gas was also attempted but it did not proceed in THF or toluene. Instead, when the reaction was performed in MeOH, **3** was smoothly converted into a pink monohydrido complex [Cp*RuBr(μ-SPr^i)$_2$RuCp*H] (**5**) at room temperature (Scheme 1).[5] The IR spectrum of **5** (KBr disk) shows a medium ν(Ru-H) band at 1968 cm^{-1}, while the singlet assignable to one hydrido proton appears at −15.06 ppm in its ^{1}H NMR spectrum. Other ^{1}H NMR data are typical of the nonsymmetric diruthenium core. Much higher reactivity of **3** towards H_2 exhibited in MeOH than in THF or toluene is noteworthy. The ^{1}H NMR spectrum of **3** recorded in CD_3OD reveals only one singlet due to the two Cp* ligands and one pair of septet



Scheme 1.

and doublet ascribable to the three SPr^i ligands.[3] This strongly suggests that **3** is converted into an ionic form $[Cp^*Ru(\mu\text{-}SPr^i)_3RuCp^*]Br$ in MeOH, which is also supported by the much greater molar conductivity of **3** observed in MeOH (1.2×10^3 S cm^2 mol^{-1}) than that in THF (1.3 S cm^2 mol^{-1}).[6] Within the triply-bridged cationic form, the vacant site required for the reaction with H_2 is probably generated more readily by the dissociation of one Ru–S bond in a bridging SPr^i ligand. This observation may correlate to our recent finding that the triply-bridged cationic complex $[Cp^*Ru(\mu\text{-}SPr^i)_2(\mu\text{-}Cl)RuCp^*][CF_3SO_3]$ is highly reactive towards various alkynes, whereas the corresponding neutral complex $[Cp^*RuCl(\mu\text{-}SPr^i)_2RuCp^*Cl]$ does not react under the same conditions.[7] Although the direct reaction of **1** with an equimolar HBr is expected to provide the more straightforward route to **5**, this resulted in the formation of an unseparable mixture of some products.

It has also been found that treatment of **5** with $PhCH_2MgCl$ and $PhCH_2CH_2MgBr$ gives the alkyl-hydrido complexes $[Cp^*RuR(\mu\text{-}SPr^i)_2RuCp^*H]$ (**6**). The products were isolated as a dark brown solid in 13% yield for R = $PhCH_2$ (**6a**) and as a red solid in 81% yield for R = $PhCH_2CH_2$ (**6b**), respectively.[8] The ^1H NMR and IR data of **6** are diagnostic of the dinuclear structure shown in Scheme 2. Interestingly, the benzyl complex **6a** in a solution state is unstable and decomposes gradually, forming the coordinatively unsaturated diruthenium complex **1** and $PhCH_3$ (Scheme 2). The ^1H NMR study of **6a** in C_6D_6 has demonstrated that the conversion of **6a** into these dinuclear elimination products proceeds almost quantitatively in two days at room temperature. This represents one of the still rare examples of the reductive elimination reaction at the well-defined dinuclear site.[9] In contrast, the phenethyl analog **6b** is quite stable and its ^1H NMR spectrum did not show any change upon heating at 50 °C for one day. Such instability specific to the benzyl ligand within the diruthenium complex has also been observed in a series of alkyl-halido complexes $[Cp^*RuR(\mu\text{-}SPr^i)_2RuCp^*X]$, for which only the benzyl complex (R = $PhCH_2$, X = Br) decomposes readily to give $PhCH_2CH_2Ph$ together with a mixture of **1** and $[Cp^*RuBr(\mu\text{-}SPr^i)_2RuCp^*Br]$.[1d] However, more recent study has shown that the benzyl-methyl complex $[Cp^*Ru(CH_2Ph)(\mu\text{-}SPr^i)_2RuCp^*Me]$ remains unaltered even when kept at 50 °C for several days.[10] Further study is now in progress to rationalize these observations and clarify the mechanism of this novel dinuclear elimination reaction.



Scheme 2.

References

1) a) M. Hidai, K. Imagawa, G. Cheng, Y. Mizobe, Y. Wakatsuki, and H. Yamazaki, *Chem. Lett.*, **1986**, 1299; b) S. Dev, K. Imagawa, Y. Mizobe, G. Cheng, Y. Wakatsuki, H. Yamazaki, and M. Hidai, *Organometallics*, **8**, 1232 (1989); c) S. Dev, Y. Mizobe, and M. Hidai, *Inorg. Chem.*, **29**, 4797 (1990); d) A. Takahashi, Y. Mizobe, H. Matsuzaka, S. Dev, and M. Hidai, *J. Organomet. Chem.*, **456**, 243 (1993).

2) a) H. Matsuzaka, Y. Mizobe, M. Nishio, and M. Hidai, *J. Chem. Soc., Chem. Commun.*, **1991**, 1011; b) H. Matsuzaka, Y. Hirayama, M. Nishio, Y. Mizobe, and M. Hidai, *Organometallics*, **12**, 36 (1993); c) M. Nishio, H. Matsuzaka, Y. Mizobe, and M. Hidai, *J. Chem. Soc., Chem. Commun.*, **1993**, 375.

3) Anal. Found: C, 43.94; H, 6.55%. Calcd for $C_{29}H_{51}S_3BrRu_2$: C, 44.77; H, 6.61%. ^{1}H NMR (THF-d_8): δ 1.58, 1.67 (s, 15H each, Cp*), 1.42, 1.45 (d, 6H each, μ-SCH*Me*$_2$), 4.39 (sep, 2H, μ-SC*H*Me$_2$), 1.04 (d, 6H, SCH*Me*$_2$), 1.29 (sep, 1H, SC*H*Me$_2$). ^{1}H NMR (CD_3OD): δ 1.98 (s, 30H, Cp*), 1.27 (d, 18H, SCH*Me*$_2$), 2.98 (sep, 3H, SC*H*Me$_2$).

4) **4a**. Anal. Found: C, 51.27; H, 6.44%. Calcd for $C_{35}H_{51}S_2BrRu_2$: C, 51.39; H, 6.28%. ^{1}H NMR (C_6D_6): δ 1.68, 1.49 (s, 15H each, Cp*), 1.61, 1.66 (d, 6H each, SCH*Me*$_2$), 5.33 (sep, 2H, SC*H*Me$_2$), 2.10 (s, 3H, C_6H_4*Me*), 7.0, 7.5 (d, 2H each, C_6H_4). **4b**. Anal. Found: C, 48.49; H, 6.68%. Calcd for $C_{32}H_{53}S_2BrRu_2$: C, 49.03; H, 6.81%. ^{1}H NMR (C_6D_6): δ 1.65, 1.49 (s, 15H each, Cp*), 1.72, 1.63 (d, 6H each, SCH*Me*$_2$), 5.24 (sep, 2H, SC*H*Me$_2$), 1.37 (s, 9H, Bu^t).

5) Yield, 56%. Anal. Found: C, 43.42; H, 6.36%. Calcd for $C_{26}H_{45}S_2BrRu_2$: C, 44.37; H, 6.44%. ^{1}H NMR (C_6D_6): δ 1.57, 1.74 (s, 15H each, Cp*), 1.40, 1.66 (d, 6H each, SCH*Me*$_2$), 3.96 (sep, 2H, SC*H*Me$_2$), −15.96 (s, 1H, RuH).

6) Molar conductivity of [Bu$^n_4$N][BF_4] in MeOH measured under the similar conditions was 0.95×10^3 S cm^2 mol^{-1}. The cationic structure of this type has been manifested previously for [Cp*Ru(μ-SPh)$_3$RuCp*]Cl by the X-ray single crystal analysis, which shows the molar conductivity of 0.81×10^3 S cm^2 mol^{-1} in CH_2Cl_2.[1a,b]

7) H. Matsuzaka, Y. Takagi, and M. Hidai, *Organometallics*, in press.

8) **6a**. Satisfactory analysis data are not yet available for this complex, since the recrystallization of the product is unsuccessful due to its instability in a solution state as described in the text. ^{1}H NMR (THF-d_8): δ 1.83, 1.45 (s, 15H each, Cp*), 1.61, 1.32 (d, 6H each, SCH*Me*$_2$), 2.78 (sep, 2H, SC*H*Me$_2$), −15.56 (s, 1H, RuH), 1.66 (s, 2H, RuCH$_2$), 7.13-7.43 (m, 5H, Ph). IR (KBr disk, cm^{-1}): 1954 [ν(Ru-H)]. **6b**. Anal. Found: C, 55.33; H, 7.29%. Calcd for $C_{34}H_{54}S_2Ru_2$: C, 56.01; H, 7.47%. ^{1}H NMR (C_6D_6): δ 1.81, 1.70 (s, 15H each, Cp*), 1.45, 1.29 (d, 6H each, SCH*Me*$_2$), 2.60 (sep, 2H, SC*H*Me$_2$), −15.60 (s, 1H, RuH), 0.44 (pseudo t, 2H, RuCH$_2$), 2.80 (pseudo t, 2H, PhC*H*$_2$), 7.10-7.43 (m, 5H, Ph). IR (KBr disk, cm^{-1}): 1931 [ν(Ru-H)].

9) See for example: J. P. Collman, L. S. Hegedus, J. R. Norton, and R. G. Finke, "Principles and Applications of Organotransition Metal Chemistry," University Science Books, Mill Valley, CA (1987) p. 333; J. R. Norton, *Acc. Chem. Res.*, **12**, 139 (1979); G. Trinquier and R. Hoffmann, *Organometallics*, **3**, 370 (1984).

10) A. Takahashi, Y. Mizobe, T. Tanase, Y. Yamamoto, and M. Hidai, manuscript in preparation.

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