Synthesis and Crystal Structures of Thiolate-Bridged Diruthenium Complexes Containing Two Olefinic Ligands

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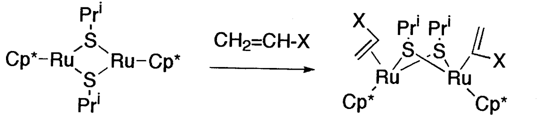
A series of thiolate-bridged dinuclear ruthenium complexes containing two electron-deficient olefinic ligands [Cp*Ru(μ-SR)$_2$(η^2-C$_2$H$_3$R')$_2$RuCp*] (R = Pr^i, Et, 2,6-C$_6$H$_3$Me$_2$ or 2,4,6-C$_6$H$_2$Me$_3$; R' = CN, COOMe or CHO) have been synthesized from Ru(II)-Ru(II), Ru(II)-Ru(III) and/or Ru(III)-Ru(III) precursors, three of which have been characterized by X-ray structural analysis.



(1)

1

3: X = CN
9: X = COOMe
10: X = CHO

Intense interest has been devoted in recent years to the chemistry of di- and multinuclear transition-metal complexes with bridging chalcogenide or chalcogenolate ligands.[1] This is not only because the structures and reactivities of this class of complexes are highly diversified, but also because they provide structural and functional models for the active sites in many metalloproteins[2] and industrially important hydrodesulfurization catalysts.[3] We have focused our attention on the synthesis and chemical properties of chalcogenolate-bridged diruthenium complexes,[4] and have revealed their unique reactivities towards alkynes,[4,5] alkyl halides,[6] aldehydes,[7] hydrazines,[8] and other metal species.[9] Indeed, alkynes undergo intriguing transformations at the bimetallic center, most notably leading to catalytic linear di- and trimerization. In contrast, studies of the interactions between the chalcogenolate-bridged diruthenium complexes and olefins are significantly fewer in number, and only the formation of the *s-trans* butadiene complexes [Cp*Ru(μ-EFc)$_2$(μ-η^2:η$^{2'}$-C$_4$H$_6$)RuCp*] (E = S, Se, or Te; Fc = ferrocenyl; Cp* = η^5-C$_5$Me$_5$)[10] and the mono(ethylene) complex [Cp*Ru(μ-SEt)$_2$(C$_2$H$_4$)RuCp*][11] have been reported so far. On the other hand, ruthenium complexes have long been known to exhibit specific activity for the catalytic dimerization of acrylonitrile, acrolein, and acrylates.[12] This background prompted us to investigate the reactivity of these specific olefins on the dinuclear ruthenium centers. Here we wish to describe the syntheses and structures of a series of thiolate-bridged diruthenium complexes which contain two electron-deficient olefinic ligands.

When the Ru(II)-Ru(II) complex [Cp*Ru(μ-SPr^i)$_2$RuCp*] (**1**) was allowed to react with acrylonitrile (5 equiv.) in ether (-78 °C - r.t., 3 h), the following complex [Cp*Ru(μ-SPr^i)$_2$(η^2-C$_2$H$_3$CN)$_2$RuCp*] (**3**) was obtained as an orange precipitate.[13] Recrystallization of the crude product from benzene-hexane gave pure **3** as orange crystals in 70% yield (Eq.1).[14] Complex **3** was also prepared in 75% yield from the reaction between the Ru(II)-Ru(III) complex [Cp*Ru(μ-SPr^i)$_3$RuCp*] (**2**) and acrylonitrile (in toluene, 60 °C, 16 h). Both Pr^{i}SCH$_2$CH$_2$CN (46%) and Pr^{i}SSPr^i (6%) were obtained from the latter reaction. Furthermore, treatment of the Ru(III)-Ru(III) complex [Cp*Ru-H(μ-SPr^i)$_2$HRuCp*] (**4**) with acrylonitrile (in benzene, 50 °C, 72 h) also gave **3** in 65% yield, although the fate of the hydrido ligands remains unclear.

The ^{1}H NMR spectrum of **3** showed a set of signals ascribed to the two acrylonitrile ligands (δ 2.76, 2.86, and 3.11), which demonstrates a considerable shift to higher field in comparison with those of free acrylonitrile. Furthermore, the ν(CN) vibration of **3** (2195 cm^{-1}) is 35 cm^{-1} lower than that of free acrylonitrile. These data suggest that both Ru(II) centers bind one molecule of acrylonitrile through the C=C bond.

The molecular structure of **3** was unambiguously determined by X-ray diffraction.[15] An ORTEP drawing of **3** is given in Figure 1. The molecule has a crystallographic 2-fold axis perpendicular to the Ru-Ru and S-S vectors. The two η^2-acrylonitrile ligands are coordinated in mutual cis configuration to the two respective ruthenium centers. A similar structure was found for the alkoxide-bridged diruthenium complex [Cp*Ru{μ-η^3-O(CH$_2$)$_2$C$_2$H$_3$}$_2$RuCp*],[16] whilst the trans geometry was reported for the two chloride-bridged complexes [Cp*Ru(μ-Cl)$_2$-(η^2-C$_2$F$_4$)$_2$RuCp*][17] and [(C$_5$Me$_4$Et)Ru(μ-Cl)$_2$(η^2-C$_2$H$_4$)$_2$Ru-(C$_5$Me$_4$Et)].[18] The long Ru···Ru distance (3.7995(7) Å) observed in **3** rules out any Ru-Ru bonding interaction.

The SEt analogue of **3**, [Cp*Ru(μ-SEt)$_2$(η^2-C$_2$H$_3$CN)$_2$-RuCp*] (**5**), was obtained in 36% yield by the reaction of [Cp*Ru(μ-SEt)$_3$RuCp*] with acrylonitrile (in toluene, 110 °C, 15 h), the spectroscopic properties[14] and crystal structure[19] of which were closely related to those of **3**. On the other hand, the

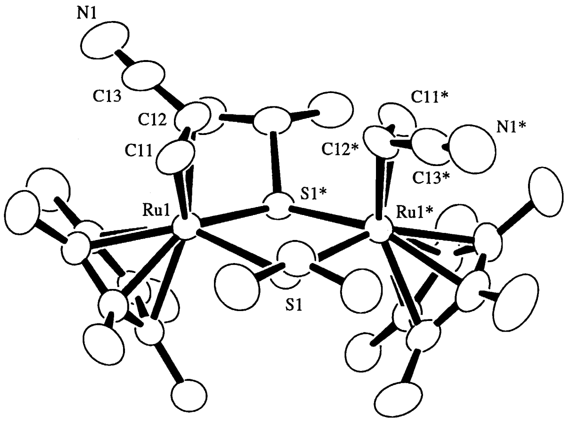


Figure 1. Molecular structure of **3**. Ru(1)-C(11) = 2.155(4), Ru(1)-C(12) = 2.187(4), C(11)-C(12) = 1.415(5), Ru(1)···Ru(1)* = 3.7995(7) Å.

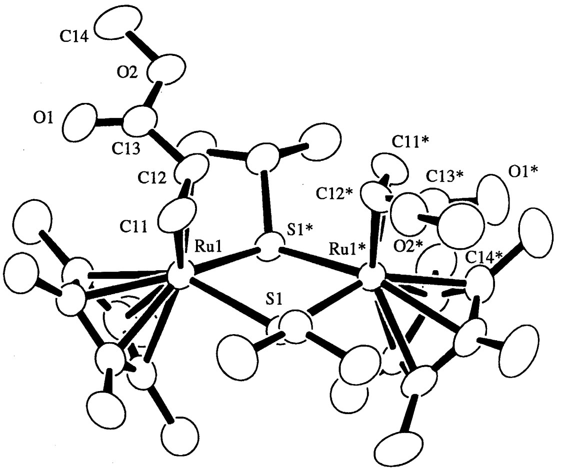


Figure 2. Molecular structure of **9**. Ru(1)-C(11) = 2.163(3), Ru(1)-C(12) = 2.219(3), C(11)-C(12) = 1.403(4), Ru(1)···Ru(1)* = 3.8042(6) Å.

arenethiolate analogues $[Cp^*Ru(\mu\text{-}SAr)_2(\eta^2\text{-}C_2H_3CN)_2RuCp^*]$ (**6**, Ar = 2,6-$C_6H_3Me_2$; **7**, 2,4,6-$C_6H_2Me_3$),[14] which were prepared from $[Cp^*Ru(\mu\text{-}SAr)_2RuCp^*]$ (**8**) in 69 - 88% yield (in ether, -78 °C - r.t., 3 h), dissociated the acrylonitrile ligands completely in benzene to regenerate **8**. The π-back bonding ability of the arenethiolate-bridged diruthenium core is considered to be insufficient to keep the η^2-acrylonitrile ligands stable in solution. It should also be noted that the corresponding ferrocenylthiolate-bridged diruthenium center coordinates butadiene to form a stable complex (*vide supra*).[10]

Diruthenium complexes of both methyl acrylate and acrolein $[Cp^*Ru(\mu\text{-}SPr^i)_2(\eta^2\text{-}C_2H_3R)_2RuCp^*]$ (**9**, R = COOMe; **10**, R = CHO)[14] were also synthesized from **1** by a similar procedure to that described for **3** (Eq.1). The crystal structure of complex **9** was determined by X-ray analysis (Figure 2).[20] Complex **9** adopts a structure with C_2 symmetry similar to **3**, in which the methyl acrylate ligands are bound to the metals with cis geometry. ^{1}H NMR measurements revealed that the methyl acrylate ligands in **9** are partially dissociated in benzene to give an equilibrium mixture of **9**, a mono(methyl acrylate) complex,[21] and **1**. Similar behavior was also observed for complex **10**. We are currently investigating the reactivity of the olefinic ligands incorporated into the diruthenium complexes.

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13 A similar reaction of **1** with acrylonitrile (100 equiv.) in THF was accompanied by polymerization of acrylonitrile (15%).

14 Satisfactory analytical data were obtained for complexes **3**, **5**-**7**, **9**, and **10**. **3**: ^{1}H NMR (C_6D_6) δ 0.74 (d, J = 6.6 Hz, 6 H), 1.02 (d, J = 6.6 Hz, 6 H), 1.29 (s, 30 H), 2.21 (sep, J = 6.6 Hz, 2 H), 2.76 (dd, J = 2.0, 8.6 Hz, 2 H), 2.86 (dd, J = 2.0, 9.9 Hz, 2 H), 3.11 (dd, J = 8.6, 9.9 Hz, 2 H); IR (KBr) 2195 cm^{-1}. **5**: ^{1}H NMR (C_6D_6) δ 0.60 (t, J = 7.3 Hz, 6 H), 1.36 (s, 30 H), 1.67 (dq, J = 13.5, 7.3 Hz, 2 H), 1.92 (dq, J = 13.5, 7.3 Hz, 2 H), 2.23 (dd, J = 2.1, 8.4 Hz, 2 H), 2.81 (dd, J = 2.1, 10.1 Hz, 2 H), 3.20 (dd, J = 8.4, 10.1 Hz, 2 H); IR (KBr) 2193 cm^{-1}. **6**: IR (KBr) 2213 cm^{-1}. **7**: IR (KBr) 2209 cm^{-1}. **9**: ^{1}H NMR (C_6D_6) δ 0.80 (d, J = 6.5 Hz, 6 H), 1.06 (d, J = 6.5 Hz, 6 H), 1.45 (s, 30 H), 3.02 (sep, J = 6.5 Hz, 2 H), 3.46 (s, 6 H), 3.52 (d, J = 7.9 Hz, 2 H), 3.86 (d, J = 10.4 Hz, 2 H), 4.19 (dd, J = 7.9, 10.4 Hz, 2 H); IR (KBr) 1694 cm^{-1}. **10**: ^{1}H NMR (C_6D_6) δ 0.84 (d, J = 6.5 Hz, 6 H), 0.90 (d, J = 6.5 Hz, 6 H), 1.25 (s, 30 H), 3.00 (sep, J = 6.5 Hz, 2 H), 3.08 (dd, J = 2.0, 10.0 Hz, 2 H), 3.52 (dd, J = 2.0, 7.6 Hz, 2 H), 4.38 (dt, J = 7.6, 10.0 Hz, 2 H), 8.38 (d, J = 7.6 Hz, 2 H); IR (KBr) 1661 cm^{-1}.

15 Crystallographic data for **3**: $C_{32}H_{50}N_2Ru_2S_2$, M = 729.02, monoclinic, $C2/c$, a = 21.405(2), b = 9.069(2), c = 17.086(1) Å, β = 100.392(8)°, V = 3262.4(6) Å^3, Z = 4, D_{calcd} = 1.484 gcm^{-3}, $\mu(MoK_\alpha)$ = 10.77 cm^{-1}, R = 0.030, R_W = 0.024 for 3022 unique reflections with $I > 3\sigma(I)$.

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19 Crystallographic data for **5**·C_6H_6: $C_{36}H_{52}N_2Ru_2S_2$, M = 779.08, triclinic, $P\bar{1}$, a = 11.761(3), b = 15.625(4), c = 11.086(4) Å, α = 104.23(2)°, β = 105.36(2)°, γ = 103.32(2)°, V = 1806(1) Å^3, Z = 2, D_{calcd} = 1.432 gcm^{-3}, $\mu(MoK_\alpha)$ = 9.78 cm^{-1}, R = 0.045, R_W = 0.034 for 4852 unique reflections with $I > 3\sigma(I)$.

20 Crystallographic data for **9**: $C_{34}H_{56}O_4Ru_2S_2$, M = 795.07, monoclinic, $C2/c$, a = 21.554(2), b = 9.559(1), c = 17.536(1) Å, β = 102.882(6)°, V = 3522.0(5) Å^3, Z = 4, D_{calcd} = 1.499 gcm^{-3}, $\mu(MoK_\alpha)$ = 10.11 cm^{-1}, R = 0.029, R_W = 0.024 for 3208 unique reflections with $I > 3\sigma(I)$.

21 Tentatively formulated as $[Cp^*Ru(\mu\text{-}SPr^i)_2(\eta^2\text{-}C_2H_3COOMe)RuCp^*]$: ^{1}H NMR ($C_6D_6$) δ 2.86 (d, J = 7.8 Hz, 1 H), 3.58 (s, 3 H), 3.80 (d, J = 11.1 Hz, 1 H), 4.53 (dd, J = 7.8, 11.1 Hz, 1 H). The Cp* and SPr^i signals were obscured by overlapping with those of complex **9**.