Synthesis of New Paramagnetic Heterodinuclear Complexes with Dithiolene Bridging Ligands, $(Ph_2C_2S_2)Fe(Cp'Ru)(\mu\text{-}Ph_2C_2S_2)_2$ ($Cp' = \eta^5\text{-}C_5H_4SiMe_3(Cp^{Si})$, $\eta^5\text{-}C_5Me_5(Cp^*)$), by Replacement of a Metal Fragment

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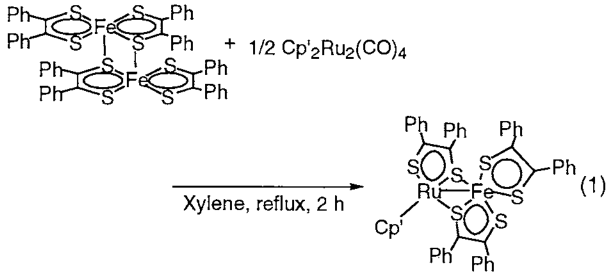
Thermal reactions of $(Ph_2C_2S_2)_4Fe_2$ with $Cp'_2Ru_2(CO)_4$(Cp' = $\eta^5\text{-}C_5H_4SiMe_3$, $\eta^5\text{-}C_5Me_5$ (Cp*)) gave new paramagnetic heterodinuclear complexes $(Ph_2C_2S_2)Fe(Cp'Ru)(\mu\text{-}Ph_2C_2S_2)_2$ bridged by two dithiolene ligands.

A number of dithiolene-bridged complexes with various transition-metals have been synthesized and structurally characterized.[1] Typical synthetic methods for them are as follows: (1) reactions of metal complexes with a sulfur source and alkyne,[2] (2) dimerization of mononuclear dithiolene complexes,[3] (3) reactions of sulfide-bridged dinuclear complexes with alkyne,[4] and (4) reactions of metal complexes with dithiodiketone or ethylenedithiol.[5] These methods all give homometallic complexes, and, to our knowledge, there is no convenient synthetic method which selectively gives heterometallic dinuclear complexes. We report here a new selective route for the synthesis of heterodinuclear group 8 metal complexes bridged by dithiolene ligands, having an odd number of metal valence electrons, via replacement of a metal fragment.

Reaction of $(Ph_2C_2S_2)_4Fe_2$ and $Cp^{Si}{}_2Ru_2(CO)_4$ (Cp^{Si} = $\eta^5\text{-}C_5H_4SiMe_3$) in 2:1 molar ratio in refluxing xylene for 2 h gave a new heterometallic dinuclear complex bridged by two dithiolene ligands, $(Ph_2C_2S_2)Fe(Cp^{Si}Ru)(\mu\text{-}Ph_2C_2S_2)_2$ (**1**),[6] in 25% yield. In a similar manner, reaction of $(Ph_2C_2S_2)_4Fe_2$ and $Cp^*{}_2Ru_2(CO)_4$ afforded $(Ph_2C_2S_2)Fe(Cp^*Ru)(\mu\text{-}Ph_2C_2S_2)_2$ (**2**)[7] in 31 % yield (eq 1). Complexes **1** and **2** are colored deep blue and are stable in air.



1: $Cp' = Cp^{Si}$
2: $Cp' = Cp^*$

In these reactions, one $(Ph_2C_2S_2)Fe$ fragment in $(Ph_2C_2S_2)_4Fe_2$ was replaced with a Cp'Ru fragment generated from $Cp'_2Ru_2(CO)_4$ ($Cp' = Cp^{Si}$, Cp*). Such a metal fragment substitution reaction is well-known in the case of metal-sulfur clusters,[8] but is unprecedented in the case of dithiolene-bridged heterodinuclear complexes.

The ^1H NMR spectra of **1** and **2** show extremely broad peaks in the range of -2–14 ppm, which are characteristic of the paramagnetic species. The FAB mass spectra of **1** and **2**, showing the molecular ion peaks at *m/z* = 1021 and 1019, respectively, as well as their elemental analysis data are consistent with the structures proposed in eq 1.

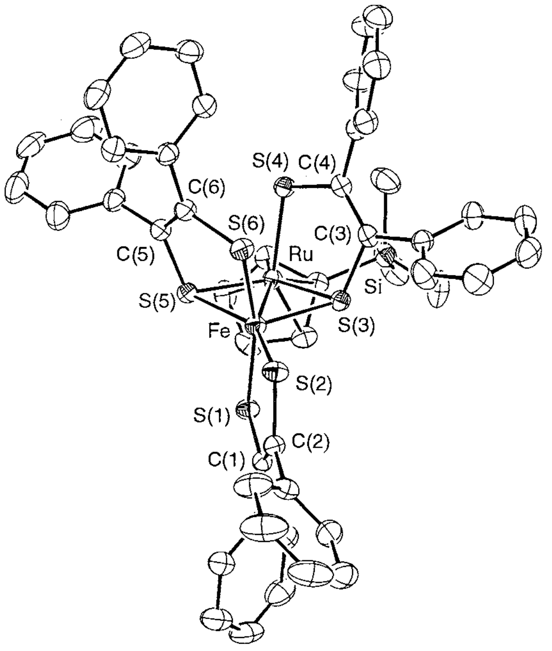


Figure 1. Molecular structure of $\mathbf{1}\cdot CH_2Cl_2$ with 50% thermal ellipsoids. The CH_2Cl_2 molecules and H atoms are omited for clarity. Selected bond lengths (Å) and angles (°): Fe–Ru 2.7472(5), Fe–S(1) 2.2012(9), Fe–S(2) 2.1750(8), Fe–S(3) 2.299(1), Fe–S(5) 2.2089(8), Fe–S(6) 2.2138(9), Ru–S(3) 2.2627(8), Ru–S(4) 2.3105(8), Ru–S(5) 2.3783(9), C(1)–S(1) 1.717(3), C(2)–S(2) 1.720(3), C(3)–S(3) 1.749(3), C(4)–S(4) 1.733(3), C(5)–S(5) 1.767(3), C(6)–S(6) 1.740(3), C(1)–C(2) 1.378(4), C(3)–C(4) 1.364(4), C(5)–C(6) 1.347(5), Ru-S(3)-Fe 74.05(3), Ru-S(5)-Fe, 73.47(3).

The molecular structure of **1** was unambiguously determined by X-ray crystallography as shown in Figure 1.[9] The $(Ph_2C_2S_2)Fe$ and $Cp^{Si}Ru$ moieties are bridged by two dithiolene ligands in the way where one of the sulfur atoms of the dithiolene ligand chelating the iron atom is further coordinated to the ruthenium atom and vice versa. All of three dithiolene ligands are nearly planar because of the delocalization of π-electrons on these chelate rings.[1b] Two bridging dithiolene ligands are mutually *cis* as in the case of $[(CpFe)_2(\mu\text{-}R_2C_2S_2)_2]$ (R = CF_3, CO_2Me).[4a,4b] The dihedral angles between the planes Fe-Ru-S(3) and Fe-Ru-S(5), the plane Fe-Ru-S(3) and the fused dithiolene ring plane, and the plane Fe-Ru-S(5) and the fused dithiolene ring plane are 169.72°, 101.92°, and 108.80°, respectively. The Fe-Ru distance (2.7472(5)

Å) is in the normal range of the Fe-Ru single bond distances.[10] The metal-sulfur bond distances of the out-of-plane coordination of bridging dithiolene ligands, namely, Fe-S(3) (2.299(1) Å) and Ru-S(5) (2.3783(9) Å), are much longer than those of the in-plane coordination (2.1750-2.2138 Å for Fe-S and 2.2627-2.3105 Å for Ru-S). This is apparently because the longer metal–sulfur bonds consist of only the coordination of dithiolene π orbitals, while the shorter, in-plane metal–sulfur bonds consist of both σ- and π-type interactions and thus have some multiple bond character. Complexes **1** and **2** are the first examples of heterometallic dinuclear complexes bridged by dithiolene ligands.

On the basis of the structure of **1** shown in Figure 1, all of the dithiolene ligands are essentially planar. Thus, with the covalent model, each dithiolene ligand is regarded to donate 4σ-electrons and simultaneously accept π-back donation from one or two metals.[11] The valence electron numbers of Fe and Ru can therefore be calculated to be 17 and 18, respectively. This is consistent with the paramagnetic character of **1**.

Table 1. Electrochemical data of **1** and **2** in 0.1 mol dm^{-3} TBAB-dichloromethane[a, b]

Complex	Couple	$E_{1/2}$/V	E_{pa}/V	E_{pc}/V
1	+1 / 0	+0.34	+0.38	+0.30
	0 / -1	-0.62	-0.58	-0.67
	-1→-2	–	–	-1.55
2	+1 / 0	+0.18	+0.21	+0.14
	0 / -1	-0.72	-0.67	-0.76
	-1→-2	–	–	-1.68

[a] *E* vs. Ag/AgNO$_3$. [b] TBAB denotes tetrabutylammonium tetrafluoroborate.

The cyclic voltammograms of **1** and **2** exhibit two reversible one-electron redox waves corresponding to +1/0 and 0/-1 couples and an irreversible one-electron reduction wave corresponding to the reduction from -1 to -2. The electrochemical data of **1** and **2** are listed in Table 1. The redox potentials of the Cp* analog **2** are more negative than those of Cp^{S1} analog **1** because the Cp* ligand is more electron-donating than the Cp^{S1} ligand. One electron redox reactions of **1** or **2** are expected to give diamagnetic species. Attempts at isolation and characterization of the redox products are now in progress.

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6 A solution of $(Ph_2C_2S_2)_4Fe_2$ (182 mg, 0.17 mmol) and $Cp^{S1}{}_2Ru_2(CO)_4$ (50 mg, 0.08 mmol) in xylene was refluxed for 2 h under a nitrogen atmosphere. After removal of a black precipitate by filtration, xylene was evaporated under reduced pressure and the residue was subjected to silica gel flash chromatography. A blue band was eluted by toluene/hexane (3 : 1). The solvent was evaporated to dryness. The blue solid was recrystallized from CH_2Cl_2/hexane to give blue crystals of 1 (43 mg, 0.04 mmol) in 25% yield. Anal. Found: C, 58.60; H, 4.31%. Calcd for $C_{51}H_{43}FeRuS_6Si$: C, 58.81; H, 4.24%. Mass (FAB, *m*-nitrobenzyl alcohol matrix, Xe) *m/z* (% rel intensity) 1021 (M^+, 87), 779 (M^+-$Ph_2C_2S_2$, 100).

7 Anal. Found: C, 60.92; H, 4.89%. Calcd for $C_{52}H_{45}FeRuS_6$: C, 61.28; H, 4.45%. Mass (FAB, *m*-nitrobenzyl alcohol matrix, Xe) *m/z* (% rel intensity) 1019 (M^+, 100), 777 (M^+-$Ph_2C_2S_2$, 36).

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9 Crystal data for **1**·CH_2Cl_2: $C_{51}H_{45}Cl_2FeRuS_6Si$; M = 1106.19, triclinic, a = 12.829(2), b = 13.299(2), c = 15.190(2) Å, α = 94.938(2)° β = 105.721(2)° γ = 94.643(2)°, V = 2470.7(4) Å^3, T = 203 K, space group $P\bar{1}$ (No.2), Z = 2, μ(Mo–Kα) = 10.20 cm^{-1}, D_c = 1.487 g cm^{-3}. The structure was solved by direct methods and refined by full-matrix least-squares techniques on all F^2 data (10937 unique reflections). $R1$ = 0.034 and $wR2$ = 0.089 for 9037 reflections with $I > 2\sigma(I)$.

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