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Synthesis of the first non-carbonyl cisoid fulvalene complexes with an Ru–Ru bond bridged by thiolate ligands

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The addition of PPh_3 to a solution which was produced by the oxidation of $[(\eta^5\text{-Cp})Ru(\mu_2\text{-}\eta^6\text{:}\eta^6\text{-}C_{10}H_8)Ru(\eta^5\text{-Cp})]^{2+}\text{-}(BF_4^-)_2$ (**1**) with *p*-benzoquinone and $BF_3{\cdot}OEt_2$ (abbreviated as *p*-Bq/BF_3) in CH_2Cl_2–CH_3CN and subsequent Zn-reduction gave the transoid Ru–Fv complex (Fv = fulvalene) formulated as $[(CH_3CN)_2(PPh_3)Ru(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)Ru(PPh_3)(CH_3CN)_2]^{2+}(BF_4^-)_2$ (**2a**) in high yield as stable yellow crystals. Treatment of **2a** with excess aryl thiols (ArSH; Ar = C_6H_5, *p*-$CH_3C_6H_4$ and *p*-ClC_6H_4), their thiolates and aryl dithiols (1,2-benzenedithiol or 3,4-toluenedithiol) or their dithiolates at room temperature afforded the Ru–Fv complexes bridged by thiolate ligands formulated as $[(PPh_3)Ru(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)(\mu_2\text{-SAr})_2Ru(PPh_3)]^{2+}(BF_4^-)_2$ (**3a**–**c**), $(ArS)Ru(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)\text{-}(\mu_2\text{-SAr})_2Ru(SAr)$ (**4a**–**c**) and $[(PPh_3)Ru(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)(\mu_2\text{-}S_2C_6H_3R)Ru(PPh_3)]^{2+}(BF_4^-)_2$ (**5a**; R = H, **5b**; R = CH_3), in high yield, respectively. Treatment of **2a** with excess *tert*-butylthiolate produced the complex $[(PPh_3)Ru(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)(\mu_2\text{-S}^t\text{Bu})_2Ru]^{2+}(BF_4^-)(S^tBu^-)$ (**6a**). In contrast with complexes **2**–**5**, a coordinatively unsaturated Ru atom was found in **6a**, which is probably formed owing to the bulkiness of the $^t\text{BuS}^-$ ligand. X-Ray analysis of complexes **3**–**6** showed the presence of an Ru^{III}–Ru^{III} single bond.

Introduction

The chemistry of the dimetallafulvalene (M_2Fv) complexes has been attractive field of investigation, because the fulvalene ligand can coordinate two transition metals in the adjacent positions, which can induce novel reactivity and enforce unusual structural features. Although a large number of carbonyl dimetallafulvalene complexes have been reported by Vollhardt and coworkers,[1] those of non-carbonyl dimetallafulvalene complexes are less,[2–9] because of the lack of good precursor for such complexes. The cisoid M_2Fv complexes are considered as potential model complexes for investigating catalytic surfaces.[10,11] Recently, we reported an Ru_2Fv complex with novel coordination mode which was prepared by the oxidation of biruthenocene with *p*-Bq/BF_3 in good yield.[12] We report here that complex $[(\eta^5\text{-Cp})Ru(\mu_2\text{-}\eta^6\text{:}\eta^6\text{-}C_{10}H_8)Ru(\eta^5\text{-Cp})]^{2+}(BF_4^-)_2$ (**1**) is a very attractive and convenient starting material for preparing various non-carbonyl cisoid Ru_2Fv complexes (Scheme 1).

Results and discussion

Preparation of transoid bis(phosphine) complex 2a

The oxidation of **1** with *p*-Bq/BF_3 at −30 °C, addition of excess PPh_3, and subsequent Zn-reduction gave an orange crystalline complex **2a** in high yield. Complex **2a** was well soluble in CH_3CN, CH_3COCH_3 and CH_3NO_2 giving yellow solutions. In the ^{1}H NMR spectrum of **2a** in CD_3NO_2, no Cp signal was observed, while two signals for the Fv ligand appeared at δ 4.36 and 4.76. The phenyl protons of PPh_3 and the methyl protons of CH_3CN were also observed at δ 7.5–7.3 and 2.08, respectively. In the ^{31}P NMR spectrum of **2a**, the phosphine ligand was found at δ 50.7, which corresponds with the reported analogous complex $RuCp(CH_3CN)_2(PPh_3)^+$ (δ 51.7) with a Ru^{II}–P bond.[13a] In combination with the results of the elemental analysis, **2a** may be assigned as $FvRu_2(CH_3CN)_4(PPh_3)_2(BF_4)_2$.

To obtain well formed single crystals, **2a** was recrystallized from CH_3CN–Et_2O in the presence of NH_4PF_6 and the X-ray analysis of the obtained complex **2b** was carried out. Selected bond distances and angles are shown in Table 1. As can be seen in Fig. 1, half of the molecule is crystallographically unique

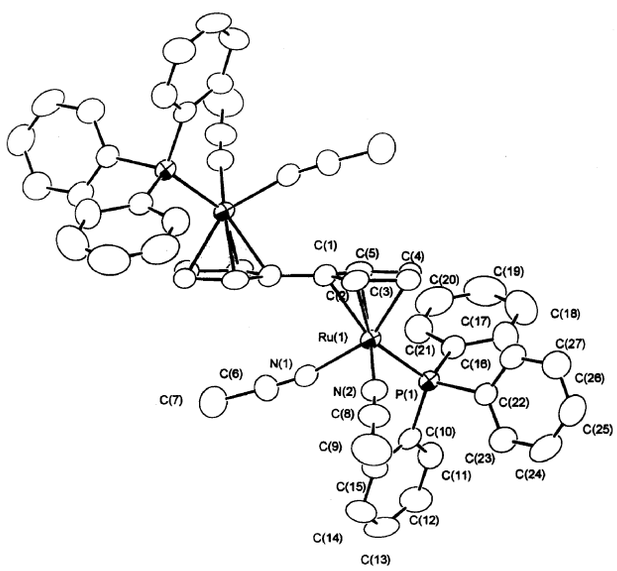

Fig. 1 ORTEP drawing of the cation $[(CH_3CN)_2(PPh_3)Ru(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)Ru(PPh_3)(CH_3CN)_2]^{2+}$ (**2b**$^{2+}$) showing 50% probability level of the thermal ellipsoids and the atom numbering scheme. For clarity all hydrogen atoms are omitted.

with the whole molecular located on an inversion center. The Fv ligand is perfectly planar and this is in sharp contrast with the complexes **3**–**6** discussed below. From the ORTEP drawing of **2b**, the interesting elimination of two Cp rings and the coordination of PPh_3 and CH_3CN to the Ru center are verified and the complex **2b** is formulated as $[(CH_3CN)_2(PPh_3)Ru^{II}\text{-}(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)Ru^{II}(PPh_3)(CH_3CN)_2]^{2+}(PF_6^-)_2$, which adopts a transoid arrangement of the Ru atoms towards the Fv ligand, like the case of **1** and biruthenocene. It is noteworthy that the loss of the Cp-ring from the complex **1** takes place easily under such mild conditions, and **2** is the first non-carbonyl half sandwich Ru_2Fv complex. The half moiety of the molecule, $(C_5H_4)Ru^{II}(PPh_3)(CH_3CN)_2]^+$, is fundamentally similar to other three-legged piano-stool complexes and the Ru–N (2.063(7), 2.069(6) Å) and Ru–P (2.340(2) Å) distances correspond with the reported values of analogous molecules.[13] The

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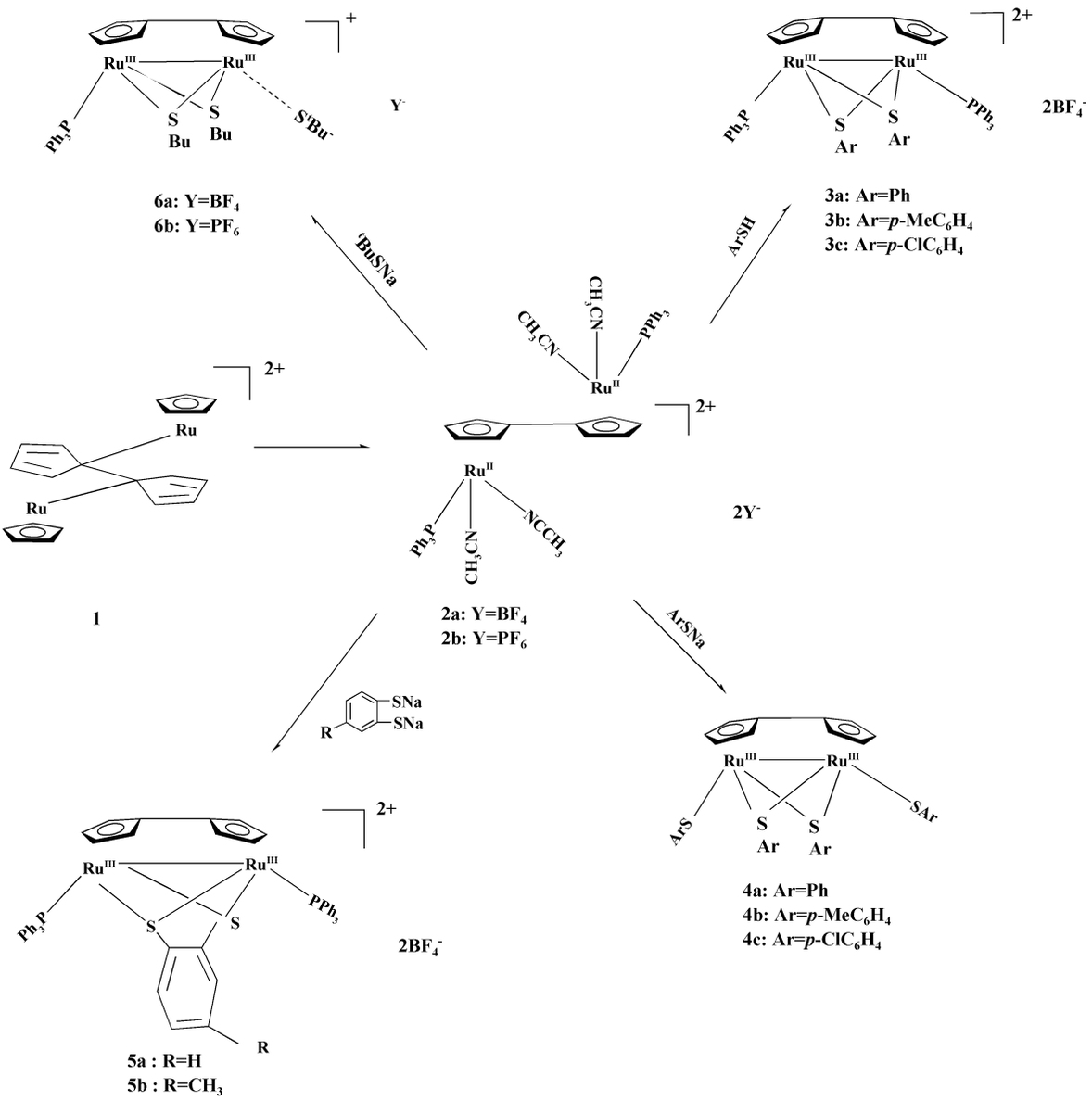


Scheme 1

average Ru–C(1–5) distance (2.123 Å) of **2b** corresponds with the values of the related half sandwich Ru^{II}–Cp complexes such as $[RuCp(CH_3CN)_2PMe_3]^+$ (2.177(5) Å)[13a] and $RuCp(CH_3CN)_3^+$ (2.135(3) Å).[13d]

A plausible mechanism to explain the formation of **2a** is shown in Scheme 2. Complex **1** is soluble in CH_3CN giving the mixed valence $Ru^{II}Ru^{IV}$ complex **A** formulated as $[CpRu^{II}(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)Ru^{IV}Cp(CH_3CN)]^{2+}$, which was verified by X-ray analysis.[13b] The oxidation of **A** with *p*-Bq/BF_3 at low temperature probably gives the unstable complex **B** with the two higher oxidation state of the Ru^{IV} atoms, although it was not isolated from the solution. Addition of PPh_3 to the solution causes the coordination of PPh_3 to the Ru^{IV} atoms and the elimination of the Cp-ring and gives the $Ru^{IV}Ru^{IV}$ complex **C**. Subsequent Zn-reduction of **C** gives the stable $Ru^{II}Ru^{II}$ complex **2a**. On the contrary, the treatment of **1** with PPh_3 in CH_3NO_2 gave the ring-attacked complex $[CpRu^{II}(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)Ru^{II}(\eta\text{-}C_5H_4PPh_3)]^+$, the structure of which was confirmed by X-ray analysis.[12] Thus the formation of an unstable intermediate complex **B** in CH_3CN at low temperature seems to be responsible for the formation of complex **2a**.

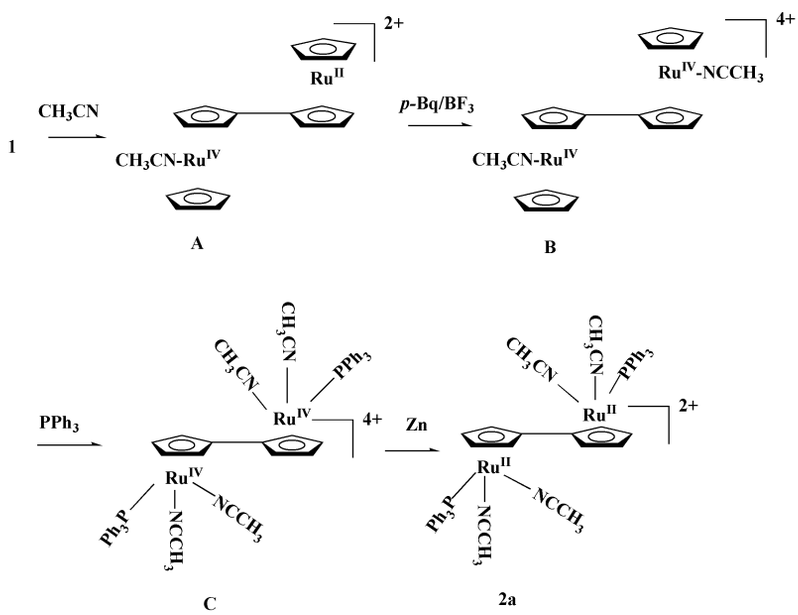
Although a large number of carbonyl Ru_2Fv complexes have been reported, the preparations of various coordination modes of the Ru_2Fv complexes are limited because of the difficulty of the selective replacement of CO from the complexes by the other nucleophiles. To extend the Ru_2Fv chemistry, the complexes **2a** and **2b** are useful as more labile precursors to synthesize a new series of Ru_2Fv complexes, because CH_3CN in **2** may be easily substituted by other nucleophiles such as halides or thiolates. So, the reactions of **2** with some typical thiols and thiolates were at first selected to verify the possibility mentioned above. As the thiolate ligands have a high ability to bridge two metal atoms, the formation of some cisoid Ru_2Fv complexes may be expected.

Reactions of 2 with arylthiols and thiolates

The reaction of **2a** with some aryl thiols (RC_6H_4SH, R = H, CH_3 and Cl) in CH_2Cl_2 gave air-stable and diamagnetic complexes **3a**–**c**, $FvRu_2(PPh_3)_2(RC_6H_4S)_2(BF_4)_2$ (R = H, CH_3 and Cl, respectively), as red crystals. The yield of **3a** increased on exposure to the air. Considering the fact that the treatment of the related Ru(II) complexes with thiols in the air gave the corresponding Ru(III) complexes accompanied by air oxidation,[14] the Ru(II) atoms in **2a** may similarly undergo air-oxidation on the addition of PhSH. The same complexes were also formed by the oxidation of **2a** with *p*-Bq/BF_3 and the subsequent addition of the thiols. In the ^1H NMR spectrum of **3a**, the proton signals of the Fv ligand are found at δ 5.39 and 4.94 at much lower field compared with those of **2a** (δ 4.76 and 4.36), suggesting the

Table 1 Selected bond distances (Å) and angles (°)

	2b	**3a**	**4a**	**4c**	**5a**	**6b**
Ru(1)–Ru(2)		2.7097(10)	2.6674(8)	2.6655(7)	2.7351(8)	2.6762(10)
Ru(1)–C(1)	2.117(6)	2.189(9)	2.195(9)	2.199(6)	2.194(8)	2.219(9)
Ru(1)–C(2)	2.171(7)	2.184(8)	2.203(8)	2.204(6)	2.190(7)	2.220(9)
Ru(1)–C(3)	2.113(8)	2.196(8)	2.216(8)	2.219(6)	2.221(8)	2.201(8)
Ru(1)–C(4)	2.135(7)	2.265(10)	2.216(8)	2.254(6)	2.219(9)	2.213(10)
Ru(1)–C(5)	2.080(7)	2.234(8)	2.232(9)	2.232(6)	2.223(8)	2.209(11)
Ru(2)–C(6)		2.179(9)	2.191(7)	2.198(5)	2.180(8)	2.161(11)
Ru(2)–C(7)		2.191(8)	2.205(8)	2.219(5)	2.218(8)	2.213(14)
Ru(2)–C(8)		2.233(8)	2.230(8)	2.234(6)	2.231(8)	2.220(12)
Ru(2)–C(9)		2.261(8)	2.233(8)	2.234(6)	2.234(8)	2.234(11)
Ru(2)–C(10)		2.233(8)	2.245(8)	2.213(6)	2.206(8)	2.228(14)
Ru(1)–S(μ_2-form)		2.353(2) (S(1))	2.355(2) (S(1))	2.342(1) (S(2))	2.349(2) (S(1))	2.384(3) (S(1))
		2.365(2) (S(2))	2.361(2) (S(2))	2.335(1) (S(3))	2.363(2) (S(2))	2.367(2) (S(2))
Ru(1)–S(η^1-form)			2.391(2) (S(4))	2.365(2) (S(1))		
Ru(2)–S(μ_2-form)		2.364(2) (S(1))	2.358(2) (S(1))	2.342(1) (S(2))	2.367(2) (S(1))	2.332(3) (S(1))
		2.371(2) (S(2))	2.350(2) (S(2))	2.335(2) (S(3))	2.346(2) (S(2))	2.338(3) (S(2))
Ru(2)–S(η^1-form)			2.401(2) (S(3))	2.355(2) (S(4))		
Ru(1)–L	2.340(2) (L = P(1))	2.380(2) (L = P(1))			2.398(2) (L = P(1))	2.357(2) (L = P(1))
	2.063(7) (L = N(1))					
	2.069(6) (L = N(2))					
Ru(2)–L		2.370(3) (L = P(2))			2.394(2) (L = P(2))	
Ru(1)–S(μ_2)–Ru(2)		70.1(1) (S(1))	68.9(1) (S(1))	69.4(1) (S(2))	70.9(1) (S(1))	69.1(1) (S(1))
		69.8(1) (S(2))	69.0(1) (S(2))	69.6(1) (S(3))	71.0(1) (S(2))	69.3(1) (S(2))
S(μ_2)–Ru–S(μ_2)		75.2(1) (Ru(1))	78.0(1) (Ru(1))	85.1(1) (Ru(1))	77.5(1) (Ru(1))	73.0(1) (Ru(1))
		74.9(1) (Ru(2))	78.2(1) (Ru(2))	85.1(1) (Ru(2))	77.5(1) (Ru(2))	74.5(1) (Ru(2))
N(1)–Ru(1)–N(2)	88.4(3)					
N(1)–Ru(1)–P(1)	98.6(2)					
N(2)–Ru(1)–P(1)	95.2(2)					



Scheme 2

formation of a cisoid Ru_2Fv complex with an Ru(III)–Ru(III) single bond.

To verify this, X-ray diffraction of **3a** was carried out. As can be seen in Fig. 2, the structure of **3a** is quite different from that of **2b**. The two Ru atoms lie at the *syn* positions of the Fv ligand and the two thiolate ligands coordinate doubly to the Ru atoms in μ_2-form. The cation of **3a** is, therefore, formulated as $[(PPh_3)Ru^{III}(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)(\mu_2\text{-}SPh)_2Ru^{III}(PPh_3)]^{2+}$. The mean Ru(1)–C (2.213 Å) and Ru(2)–C (2.219 Å) distances of the Fv ligand are significantly longer than that of **2b** (2.123 Å), suggesting the presence of the higher oxidation state Ru(III) atoms in **3a**, and the two unsaturated Ru(III) atoms require an Ru(III)–Ru(III) bond to achieve an 18-electron configuration. The Ru(III)–Ru(III) distance (2.7097(10) Å) is closer to the value found for thiolate-bridged diruthenium complexes[15] such as $[RuCp^*_2(SPh)_3]^+$ (2.630(1) Å).[15d] The Ru–Ru bond leads to a large non-planarity of the Fv ligand (the dihedral angle between the η^5-C_5H_4 planes of the Fv ligand is 150.8° which is similar to the value reported for $Ru_2Fv(CO)_4$ (151.5°)[1c] and $Ru_2Fv(CO)_3(C_2H_2)$ (148.4°)[1i]). The Ru–S(μ_2) bond lengths (2.35–2.37 Å) and the Ru–S(μ_2)–Ru bond angles (69.8 and 70.1°) are nearly coincident with the values of analogous thiolate-bridged biruthenium complexes[15] such as $[Ru_2Cp^*_2(SPh)_3]^+$ (2.33–2.36 Å and 66–70°, respectively).[15d] The Ru_2S_2 core adopts a butterfly structure and the dihedral angle (core angle) between the Ru(1)–S(1)–Ru(2) and Ru(1)–S(2)–Ru(2) planes is 96.1°, which is smaller than that of the analogous thiolate- and alkoxide-bridged biruthenium complexes.[15,16] It is of note that the benzene ring of one thiolate ligand is arranged nearly parallel and that of the other is perpendicular to the Fv ligand. This is in sharp contrast with the complex **4a** (*vide infra*).

Treatment of **2a** with excess aryl thiolates (RC_6H_4SNa,

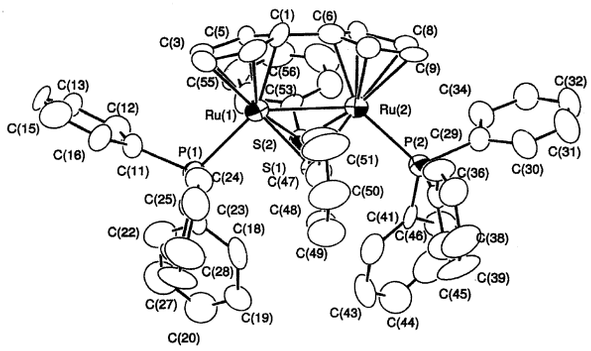


Fig. 2 ORTEP drawing of cation $[(PPh_3)Ru(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)(\mu_2\text{-}SC_6H_5)_2Ru(PPh_3)]^{2+}$ (**3a**$^{2+}$), showing 50% probability level of the thermal ellipsoids and the selective atom-numbering scheme. For clarity all hydrogen atoms are omitted.

R = H, CH_3 and Cl) in CH_2Cl_2 gave the diamagnetic and neutral Ru(III) thiolate complexes **4a**–**c**, $FvRu_2(RC_6H_4S)_4$ (R = H, CH_3 and Cl, respectively), in high yield. In the ^{1}H NMR spectrum of **4a**, the phenyl protons of PPh_3 found in **3a** were not observed, suggesting all the CH_3CN and PPh_3 ligands of the starting complex **2a** were substituted by the stronger ArS^- ligands. Two Fv-proton signals appeared at δ 5.63 and 3.09, implying the presence of two mirror planes in the Fv-ligand. The fact that one of them is observed at lower field suggests a structure similar to **3a** for **4a**. However, the large chemical shift difference ($\Delta\delta$ = 2.54 ppm) of the Fv protons compared with that of complex **3a** ($\Delta\delta$ = 0.45 ppm) and anomalous higher-field signal at δ 3.09 may suggest a possibility of an μ_2-η^4:η^4-mode in the Fv ligand.

Just recently, the interesting μ_2-η^4:η^4-mode cisoid Rh–Fv complex, $[Rh_2IFv(PMe_3)_4]I$, with an Rh–I–Rh bond was reported,[17] in which the Fv protons are found at δ 5.59 and 2.52. These proton signals are very similar to those found in **4a**. To confirm the structure of **4a**, X-ray diffraction was carried out and the ORTEP view was depicted in Fig. 3. Two thiolate

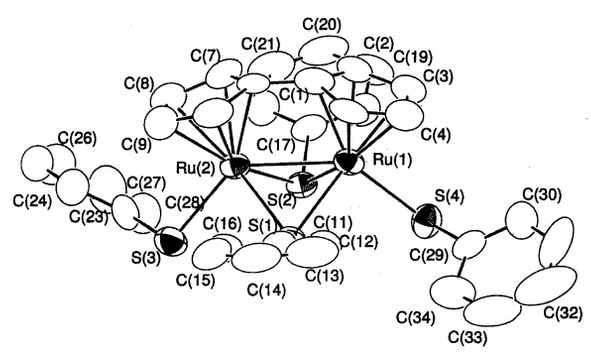


Fig. 3 ORTEP drawing of $(C_6H_5S)Ru(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)(\mu_2\text{-}SC_6H_5)_2Ru(SC_6H_5)$ (**4a**) showing 50% probability level of the thermal ellipsoids and the selective atom-numbering scheme. For clarity all hydrogen atoms are omitted.

ligands coordinate to the Ru atoms in μ_2-form and the other two thiolate ligands coordinate in η^1-form. The mean Ru–S(μ_2) distance (2.356 Å, which is closer to the value of **3a**, (2.363 Å)) is smaller than the value of Ru–S(η^1) (2.396 Å). The structure of the cation of **4a** has two mirror planes around the $Ru_2Fv(\mu_2\text{-}SPh)_2$ moiety and this is in sharp contrast with the complex **4c** (*vide infra*). The Ru–Ru distance (2.6674(8) Å) is shorter than that of **3a** (2.7097(10) Å) and the core angle (99.7°) of the Ru_2S_2 is similar to the value of **3a**. The Fv ligand has non-planarity similarly as found in **3a**, the dihedral angle (147.1°) between the two C_5H_4 planes is similar to that of **3a**.

The X-ray results of **4a** are in sharp contrast with those found in the μ_2-η^4:η^4-mode complex, $[Rh_2IFv(PMe_3)_4]I$, in three ways. (i) The Fv ligand of complex $[Rh_2IFv(PMe_3)_4]I$ is perfectly planar. (ii) The C_{ipso}–C_{ipso} bond distance (1.445(13) Å, C(1)–C(6)) of the Fv ligand in **4a** is much longer the corresponding distance (1.38(2) Å) of $[Rh_2IFv(PMe_3)_4]I$. (iii) The Ru–C_{ipso} distances (2.195(9) Å for Ru(1)–C(1), 2.191(7) Å for Ru(2)–C(6)) in **4a** are much smaller than the corresponding distances (2.5114(14) and 2.563(12) Å) in $[Rh_2IFv(PMe_3)_4]I$. Consequently, the Fv in **4a** is in μ_2-η^5:η^5-$C_{10}H_8$-form rather than the μ_2-η^4:η^4-$C_{10}H_8$-form and the complex **4a** is formulated as $(\eta^1\text{-PhS})Ru^{III}(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)(\mu_2\text{-PhS})_2Ru^{III}(\eta^1\text{-SPh})$ and this is the first example of a cisoid neutral non-carbonyl Fv–Ru complex. Unlike the case of **3a**, the two benzene rings of the bridging thiolate ligands in **4a** are arranged nearly parallel to the Fv ligand plane in the solid state. This conformation may be retained in solution because the rotation around the S–C_{ipso} bond of the bridging thiolate ligand is likely to be restricted by the presence of the terminal thiolate ligand. As a result, the α protons in the Fv-ligand are located in the shielding zone of the benzene ring of the bridging thiolate, resulting in the high field shifts mentioned above (δ 3.09).

The ^{1}H NMR spectrum of **4c** was quite different from those of **4a** and **4b**, in which four signals at δ 5.75, 5.71, 5.27 and 3.56 were found for the Fv ligand, suggesting lower symmetry around the Ru atoms. To clarify the structure of **4c**, X-ray analysis has been undertaken. As can be seen in Fig. 4, the

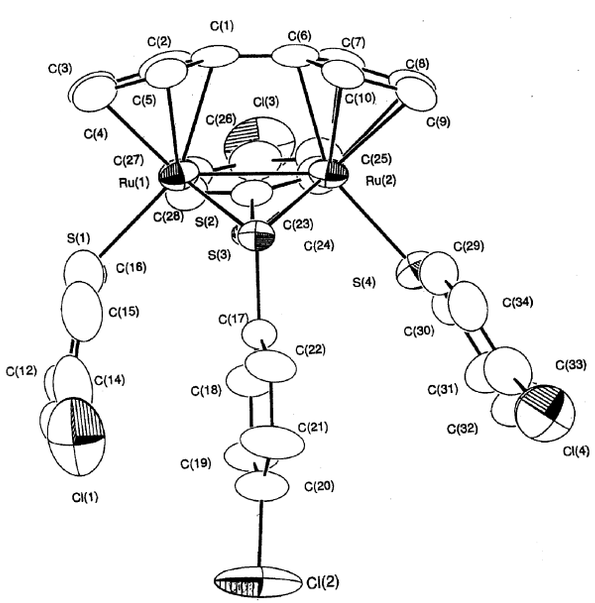


Fig. 4 ORTEP drawing of $(ClC_6H_4S)Ru(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)(\mu_2\text{-}SC_6H_4Cl)_2Ru(SC_6H_4Cl)$ (**4c**), showing 50% probability level of the thermal ellipsoids and the selective atom-numbering scheme. For clarity all hydrogen atoms are omitted.

fundamental structure of **4c** is similar to that of **4a**, with two thiolate ligands coordinated in μ_2-form and the other two in η^1-form to the Ru atoms. The Ru–Ru distance (2.6655(7) Å) and the dihedral angle between the Cp planes (147.6°) are normal. Unlike the case of **4a**, typical π-stacking of arenes is found between the three thiolate benzene rings defined by [C(11)–C(16)], [C(17)–C(22)] and [C(29)–C(34)], and are roughly perpendicular to the Fv ligand. The remaining benzene ring, [C(23)–C(28)], is nearly parallel to the Fv-ligand. The shortest C ··· C distance between the benzene rings of the stacked thiolate ligands is 3.238(8) Å [C(11) ··· C(17)], which is considerably smaller than twice the value (3.40 Å) of the van der Waals radius of a carbon atom. Thus, these three stacking thiolate ligands interact spatially each other *via* p_π–p_{π^*} interactions. This structure of **4c** in the solid state may be retained in the solution, which leads to the four proton signals of the Fv ligand in **4c**, as mentioned above. It is also noteworthy that such a conformation of the thiolate ligands results in a large core

angle (110.8°) of the Ru_2S_2 moiety in **4c**, compared with those of **3a** (96.1°) and **4a** (99.7°).

Reaction of 2 with aryl dithiols and dithiolates

There are only a few studies on benzenedithiolate complexes compared with those of aryl monothiolate complexes.[18–22] The reaction of **2a** with 1,2-benzenedithiol and the related dithiols is attractive because 1,2-benzenedithiolate has a high chelating ability for metal atoms. The reaction of **2a** with excess 1,2-benzenedithiol or 3,4-toluenedithiol in CH_2Cl_2 under air gave the air-oxidized diamagnetic Ru(III) thiolate complexes $[Fv(RuPPh_3)_2(C_6H_4S_2)](BF_4)_2$ (**5a**) and $[Fv(RuPPh_3)_2(CH_3C_6H_3S_2)](BF_4)_2$ (**5b**), respectively. The reaction of **2a** with the sodium 1,2-benzenedithiol or 3,4-toluenedithiolate gave the same complexes **5a** (83%) and **5b** (85%), respectively, in high yield. Complex **5a** was also prepared by the oxidation of **2a** with *p*-Bq/BF_3 and the subsequent addition of sodium 1,2-benzenedithiolate. In the ^{1}H NMR spectrum of **5a**, two proton signals of Fv ligand are found at δ 5.48 and 5.08, implying the presence of two mirror planes in the Fv ligand. The most interesting feature in the ^{1}H NMR spectrum of **5a** was found in the proton signals (δ 5.65 and 5.43) of the dithiolate ligand. Both signals are at much higher field compared with those of free 1,2-benzenethiol (δ 7.32) and of reported 1,2-benzenethiolate complexes (6.6–7.4).[18] A similar higher field shift of the thiolate ligand protons was found in **5b** (δ 5.51, 5.46, 5.16). To the best our knowledge, these higher field shifts are the largest found in 1,2-benzenedithiol and related thiol complexes.

In order to rationalize this novel phenomenon, X-ray diffraction of **5a** was carried out. As seen in Fig. 5, the fundamental

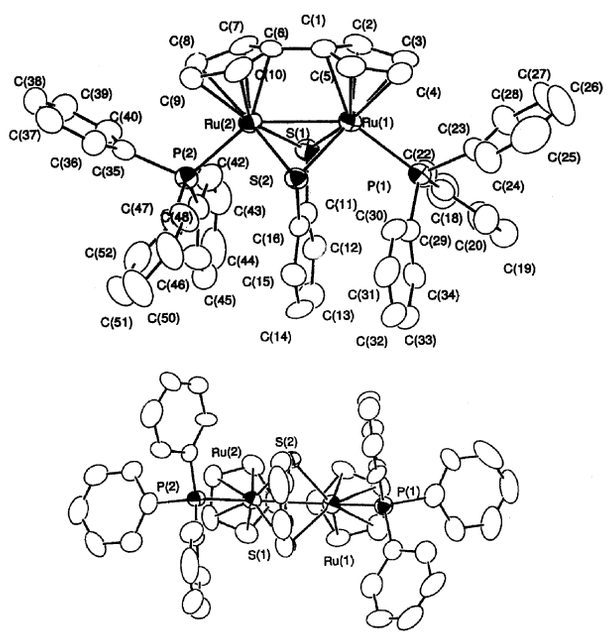


Fig. 5 ORTEP drawing of $[(PPh_3)Ru(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)(\mu_2\text{-}S_2C_6H_4)\text{-}Ru(PPh_3)]^{2+}$ (**5a**$^{2+}$), showing 50% probability level of the thermal ellipsoids and the selective atom-numbering scheme. Top: general view. Bottom: bottom view. For clarity, all hydrogen atoms are omitted.

structure of **5a** is similar to that of **3a**, *i.e.*, two sulfur atoms in the 1,2-benzenedithiolate ligand coordinate to the two Ru atoms in the μ_2-form and the cation is formulated as $[(PPh_3)Ru^{III}(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)(\mu_2\text{-}1,2\text{-}C_6H_4S_2)Ru^{III}(PPh_3)]^{2+}$. The Ru–Ru distance (2.7351(8) Å), the mean Ru–S(μ_2) distance (2.356 Å), the dihedral angle (150.3°) between the η^5-C_5H_4 planes of the Fv ligand and the core angle (100.4°) of the Ru_2S_2 moiety are normal. The typical π-stacking of arenes is found in the benzene ring planes of the dithiolate and PPh_3 ligands. From the bottom view of Fig. 5, it is seen that the benzene rings in the dithiolate ligand defined by [C(11)–C(16)] lie between the rings defined by [C(29)–C(34)] and [C(41)–C(46)] of PPh_3 groups. The three planes are essentially parallel each other (the dihedral angle of the planes are within *ca.* 4.0°) and perpendicular to the Ru–Ru vector. The C(16) ··· C(29) and C(11) ··· C(41) distances are 3.15(1) and 3.13(1) Å, respectively. Moreover, the three stacking benzene planes with layer structure are slightly slipped relative to each other. As the result, the benzene protons of the dithiolate ligand in **5a** appear at much higher field (δ 5.2–5.7). On further addition of sodium 1,2-dithiolate to the solution of **5a**, no evidence for the elimination of the PPh_3 ligands of **5a** was found. The fact is in sharp contrast with the reactions of **2a** with aryl monothiol and monothiolate, which gave different products (**3** and **4**, respectively). These tight π-stacking of the arenes found in **5a** may prevent the elimination of the PPh_3 ligand by addition of excess sodium 1,2-benzenedithiolate.

Many interesting reactions of the complexes $Cp^*Ru(SR)_n\text{-}RuCp^*$ (R = Et, ^{i}Pr and ^{t}Bu; n = 2 and 3) with some alkynes have been reported,[15b,e,h] whereas no reaction of **3**, **4** and **5** with diphenylacetylene and terminal alkynes (RC≡CH, R = Ph, C_4H_9 and C_5H_{11}) were found in various conditions, probably because of the presence of the two coordinatively saturated Ru atoms in **3**, **4** and **5**.

Reaction of 2 with *tert*-butylthiolate

Much attention has been paid to the chemistry of binuclear thiolate Ru–Cp* complexes formulated as $Cp^*Ru(\mu_2\text{-}S^iPr)_n\text{-}RuCp^*$ (n = 2 and 3) in which one or two unsaturated Ru atoms exist potentially. Due to the presence of unsaturated Ru atoms, the reactions of the complexes with some terminal alkynes gave a great variety of products.[15e,h,i] To prepare the similar unsaturated Ru_2Fv complexes, the reaction of **2** with an excess of ^{t}BuSH (one of the typical bulky alkylthiols) was carried out, but no reaction was observed as in the case of $[Cp^*RuCl_2]_2$ with ^{t}BuSH.[15d] By contrast, the reaction of **2a** with excess ^{t}BuSNa in CH_2Cl_2 afforded the less stable diamagnetic Ru(III) complex $FvRu_2(^tBuS)_3(PPh_3)BF_4$ (**6a**) in 32% yield. In the ^{1}H NMR spectrum of **6a**, four proton signals of the Fv ligand at δ 5.74, 5.32, 4.91 and 4.59 and two proton signals of the ^{t}BuS$^-$ ligand at δ 1.35 (coordinated), 0.77 (free) are found, suggesting a less symmetrical geometry around the Fv-ligand and the presence of an unsaturated Ru atom. The ^{13}C NMR spectrum of **6a** also led to the same conclusions.

To obtain well formed single crystals, the PF_6 salt **6b** was obtained by recrystallization of **6a** from CH_3CN–Et_2O in the presence of NH_4PF_6. The structure was determined by X-ray crystallography and the ORTEP plot is shown in Fig. 6. The

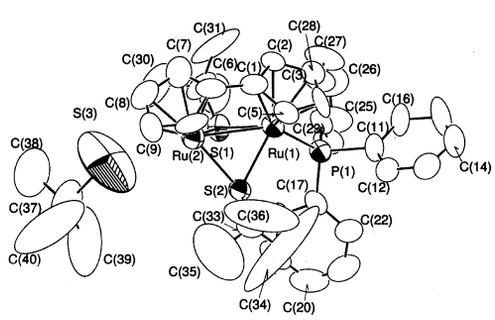


Fig. 6 ORTEP drawing of $[(PPh_3)Ru(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)(\mu_2\text{-}S^tBu)_2Ru]^{2+}$ (**6b**$^{2+}$) ($S^tBu)^-$, showing 50% probability level of the thermal ellipsoids and the selective atom-numbering scheme. For clarity all hydrogen atoms are omitted.

fundamental structure of **6b** is quite different from the former complexes **3**–**5**. Two coordination modes of the Ru atoms are found; one is the 18-electron configuration around the Ru(1) atom and the other is the 16-electron configuration around the Ru(2) atom and the complex **6b** is formulated as $[(PPh_3)\text{-}$

$Ru^{III}(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)(\mu_2\text{-}S^tBu)_2Ru^{III}]^{2+}(BF_4^-)(S^tBu^-)$ with two different coordination geometries of the Ru atoms in the molecule.

The Ru–Ru (2.6762(10) Å) distances, the Ru–S–Ru (69.1 and 69.3°) and S–Ru–S (73.0 and 74.5°) angles correspond with those of reported analogous *tert*-butylthiolate–Ru complexes [16] and the present complexes **3**–**5**. The dihedral angle (147.9°) between the η^5-C_5H_4 planes of the Fv ligand and the core angle (93.7°) of the Ru_2S_2 moiety are normal. The Ru(1)–S(μ_2) distances (2.384(3), 2.367(2) Å) are somewhat longer than the values of Ru(2)–S(μ_2) (2.332(3) and 2.338(3) Å). Although the Ru(2) ··· S(3) distance (3.21(1) Å) is too long to form a bond but it is possible to cause strong interaction between the atoms. The coordinatively unsaturated Ru(2) atom requires the coordination of the $^tBuS(3)^-$ anion to satisfy the 18-electron configuration, yet the $^tBuS(3)^-$ anion remains in an outer sphere coordination site because of the bulkiness of $^tBuS^-$ ligand. Actually, the S(3) ··· C(8) (3.07(2) Å) distance is much smaller than the sum (3.55 Å) of the van der Waals radius of the S and C atoms. The low yield of **6** compared with that of complexes **3**–**5** must be due to the presence of the unsaturated Ru atom (some unidentified precipitates were formed during the reaction of **2** and the thiolate).

Conclusion

From all the results of the present studies, it can be concluded that complex **2** is an excellent precursor of a new series of Fv–diruthenium complexes. The reactions of **2** with some aryl thiols and thiolates gave the cisoid thiolate-bridged diruthenium Fv-complexes (**3**–**5**) with the direct Ru^{III}–Ru^{III} bond consisting of two saturated Ru atoms. On the contrary, the reaction of **2** with sodium *tert*-butylthiolate gave the thiolate-bridged diruthenium–Fv complex **6** with one coordinatively unsaturated (16e) Ru atom. The latter is expected to be a good precursor to synthesize another new series of Ru_2–Fv complexes and investigation along such lines is in progress.

Experimental

General

All solvents were dried and distilled before use. All chemicals were standard regent grade and used without further purification. ^{1}H-, ^{13}C- and ^{31}P-NMR spectra were recorded on a Bruker AM-400 instrument using TMS as an internal standard. ^{31}P NMR signals were referred to external 85% H_3PO_4 as standard. Abbreviations: s = singlet; d = doublet; t = triplet; m = multiplet.

Syntheses

$[(CH_3CN)_2(PPh_3)Ru(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)Ru(PPh_3)(CH_3CN)_2](BF_4)_2$ (2a). To a solution of **1** (2.2 g, 3.5 mmol) and *p*-benzoquinone (430 mg) in CH_3CN (50 ml) and CH_2Cl_2 (50 ml) was added a solution of $BF_3{\cdot}Et_2O$ (9 ml) in CH_2Cl_2 (30 ml) at −30 °C. The solution was stirred for 1 h and then a solution of PPh_3 (4.5 g) in CH_2Cl_2 (50 ml) was added. The solution was stirred for 3 h at −30 °C, then warmed to room temperature followed by stirring for 20 h. To the resulting red–orange solution, Zn dust (1 g) was added and the mixture was stirred for 5 h at 40 °C, during which Ru(III) species were fully reduced and a yellow solution was obtained. After the Zn dust had been filtered off, the addition of diethyl ether (120 ml) to the filtrate formed yellow precipitates **2a** (3.4 g; 82%), mp >220 °C (decomp.) (Found: C, 54.60; H, 4.43; N, 4.79. $C_{54}H_{50}B_2F_8N_4P_2Ru_2$ requires C, 54.39; H, 4.95; N, 4.66%); δ_H (CD_3NO_2) 7.5–7.3 (30H, m, PPh_3), 4.76 (4H, t, η-C_5H_4), 4.36 (4H, t, η-C_5H_4) and 2.08 (12H, br, CH_3CN); δ_C (CD_3NO_2) 132.7 (d, 43 Hz, *ipso*-Ph), 134.6 (d, 11 Hz, *o*-Ph), 129.4 (br, *p*-Ph), 127.5 (d, 9 Hz, *m*-Ph), 126.8 (s, CN), 89.3 (*ipso*-C_5H_4), 75.9 (η-C_5H_4), 73.8 (η-C_5H_4) and 1.3 (s, CH_3CN); δ_P (CD_3CN) 50.7.

$[(PPh_3)Ru(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)(\mu_2\text{-}SC_6H_5)_2Ru(PPh_3)](BF_4)_2$ (3a). PhSH (20 mg) was added to a solution of **2a** (107 mg, 0.090 mmol) in CH_2Cl_2 (50 ml). The mixture was stirred for 20 h in air and then the solvent was evaporated under reduced pressure. The residue was chromatographed on silica gel by elution with CH_3CN–Et_2O (1:1) to give **3a** as red crystals (94 mg, 84%), mp > 210 °C (Found: C, 55.61; H, 4.12. $C_{58}H_{48}B_2F_8P_2Ru_2S_2$ requires C, 55.87; H, 3.88%); δ_H ($CDCl_3$) 7.5–7.2 (36H, m, PPh_3 and SPh), 6.65 (4H, t, SPh), 5.39 (4H, t, η-C_5H_4) and 4.94 (4H, t, η-C_5H_4); δ_C (CD_3CN) 135.2 (*ipso*-Ph), 134.2 (t, 48 Hz, *o*-Ph), 132.3 (br, *p*-Ph), 129.3 (t, 48 Hz, *m*-Ph), 131.8 (*ipso*-SPh), 131.2 (SPh), 130.3 (SPh), 93.6 (η-C_5H_4), 88.6 (η-C_5H_4) and 85.4 (*ipso*-C_5H_4); δ_P ($CDCl_3$) 32.6.

$[(PPh_3)Ru(\mu_2\text{-}\eta^5\eta^5\text{-}C_{10}H_8)(\mu_2\text{-}SC_6H_4CH_3)_2Ru(PPh_3)](BF_4)_2$ (3b). This complex was prepared in 81% yield using **2a** and *p*-$CH_3C_6H_4SH$ according to the same method as that described above, mp > 210 °C (Found: C, 56.41; H, 4.42. $C_{60}H_{52}B_2F_8P_2Ru_2S_2$ requires C, 56.53; H, 4.11%); δ_H ($CDCl_3$) 7.4–7.0 (34H, m, PPh_3 and $SC_6H_4CH_3$), 6.51 (4H, d, $SC_6H_4CH_3$), 5.36 (4H, t, η-C_5H_4), 4.83 (4H, t, η-C_5H_4) and 2.27 (6H, s, CH_3); δ_P ($CDCl_3$) 32.7.

$[(PPh_3)Ru(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)(\mu_2\text{-}SC_6H_4Cl)_2Ru(PPh_3)](BF_4)_2$ (3c). This complex was prepared in 79% yield using **2a** and *p*-ClC_6H_4SH according to the same method as that described above, mp > 210 °C (Found: C, 52.75; H, 3.25. $C_{58}H_{46}B_2F_8Cl_2P_2Ru_2S_2$ requires C, 52.95; H, 3.52%); δ_H ($CDCl_3$) 7.5–7.1 (34H, m, PPh_3 and SC_6H_4Cl), 6.51 (4H, d, SC_6H_4Cl), 5.45 (4H, t, η-C_5H_4) and 4.70 (4H, t, η-C_5H_4); δ_P ($CDCl_3$) 32.5.

$(\eta^1\text{-}C_6H_5S)Ru(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)(\mu_2\text{-}SC_6H_5)_2Ru(\eta^1\text{-}SC_6H_5)$ (4a). A solution of **2a** (107 mg, 0.090 mmol) in CH_2Cl_2 (50 ml) was treated with a solution of PhSNa prepared from sodium (115 mg, 5 mmol) and PhSH (0.1 g) in MeOH (2 ml). The mixture was stirred for 20 h and then the solvent was evaporated under reduced pressure. The residue was chromatographed on silica gel by elution with CH_2Cl_2 to give **4a** (55 mg, 80%) as dark red crystals, mp 138 °C (Found: C, 53.53; H, 3.52. $C_{34}H_{28}Ru_2S_4$ requires C, 53.24; H, 3.68%); δ_H ($CDCl_3$) 7.98 (2H, d, SPh), 7.50–6.70 (16H, m, SPh), 6.52 (2H, d, SPh), 5.63 (4H, t, η-C_5H_4) and 3.09 (4H, t, η-C_5H_4).

$(\eta^1\text{-}CH_3C_6H_4S)Ru(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)(\mu_2\text{-}SC_6H_4CH_3)_2Ru(\eta^1\text{-}SC_6H_4CH_3)$ (4b). This complex was prepared in 72% yield using **2a** and *p*-$CH_3C_6H_4SH$ by the method described above, mp 141 °C (Found: C, 55.35, H, 4.51. $C_{38}H_{36}Ru_2S_4$ requires C, 55.45; H, 4.41%); δ_H ($CDCl_3$) 7.80 (4H, d, $SC_6H_4CH_3$), 6.98 (4H, d, $SC_6H_4CH_3$), 6.59 (4H, d, $SC_6H_4CH_3$), 6.33 (4H, d, $SC_6H_4CH_3$), 5.61 (4H, t, η-C_5H_4) and 3.07 (4H, t, η-C_5H_4), 2.26 (6H, s, $SC_6H_4CH_3$), 2.14 (6H, s, $SC_6H_4CH_3$).

$(\eta^1\text{-}ClC_6H_4S)Ru(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)(\mu_2\text{-}SC_6H_4Cl)_2Ru(\eta^1\text{-}SC_6H_4Cl)$ (4c). This complex was prepared in 72% yield using **2a** and *p*-ClC_6H_4SH according to the method described above, mp 155 °C (Found: C, 45.24; H, 2.72. $C_{34}H_{24}Cl_4Ru_2S_4$ requires C, 45.14; H, 2.67%); δ_H ($CDCl_3$) 7.48 (2H, d, SC_6H_4Cl), 7.15 (4H, m, SC_6H_4Cl), 6.95–6.86 (8H, m, SC_6H_4Cl), 6.80 (2H, d, SC_6H_4Cl), 5.75 (2H, t, η-C_5H_4), 5.71 (2H, t, η-C_5H_4), 5.27 (2H, t, η-C_5H_4) and 3.56 (t, 2H, η-C_5H_4).

$[(PPh_3)Ru(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)(1,2\text{-}\mu_2\text{-}C_6H_4S_2)Ru(PPh_3)](BF_4)_2$ (5a). This complex was prepared in 83% yield using **2a** and benzene-1,2-dithiol according to the method described for **4a**, mp > 220 °C (Found: C, 53.35; H, 3.96. $C_{52}H_{42}B_2F_8P_2Ru_2S_2$ requires; C, 53.44; H, 3.62%); δ_H ($CDCl_3$) 7.5–7.4 (30H, m, PPh_3), 5.65 (2H, virtual quartet, $S_2C_6H_4$), 5.48 (4H, t, η-C_5H_4),

5.43 (2H, virtual quartet, $S_2C_6H_4$) and 5.08 (4H, t, η-C_5H_4); δ_C (CD_3CN) 147.5 (t, *ipso*-1,2-dithiol), 135.2 (br, *ipso*-Ph), 135.0 (m, *o*-Ph), 132.9 (br, *p*-Ph), 129.9 (br, *m*-Ph), 129.8 ($S_2C_6H_4$), 127.4 ($S_2C_6H_4$), 94.0 (η-C_5H_4), 85.9 (*ipso*-η-C_5H_4) and 84.5 (η-C_5H_4); δ_P ($CDCl_3$) 45.2.

[(PPh$_3$)Ru(μ$_2$-η^5:η^5-C$_{10}$H$_8$)(3,4-μ$_2$-C$_6$H$_3$CH$_3$S$_2$)Ru(PPh$_3$)](BF$_4$)$_2$ (5b). This complex was prepared in 85% yield using **2a** and 3,4-toluenedithiol according to the method described for **4b**, mp >220 °C (Found: C, 53.65; H, 3.96. $C_{53}H_{44}B_2F_8P_2Ru_2S_2$ requires C, 53.82; H, 3.75%); δ_H ($CDCl_3$) 7.5–7.4 (30H, m, PPh_3), 5.50 (2H, t, η-C_5H_4), 5.47 (2H, t, η-C_5H_4), 5.16 (2H, t, η-C_5H_4), 5.03 (2H, t, η-C_5H_4), 5.51 (1H, d, $S_2C_6H_3CH_3$), 5.46 (1H, d, $S_2C_6H_3CH_3$), 5.16 (1H, s, $S_2C_6H_3CH_3$) and 1.49 (3H, s, $S_2C_6H_3CH_3$); δ_C (CD_3CN) 147.4 (t, *ipso*-$S_2C_6H_3CH_3$), 144.1 (t, *ipso*-$S_2C_6H_3CH_3$), 136.9 (t, *ipso*-$S_2C_6H_3CH_3$), 137.3 (br, *ipso*-Ph), 134.6 (d, *o*-Ph), 132.1 (br, *p*-Ph), 129.0 (d, *m*-Ph), 130.8 ($S_2C_6H_3CH_3$), 128.6 ($S_2C_6H_3CH_3$), 127.5 ($S_2C_6H_3CH_3$), 94.0 (η-C_5H_4), 93.2 (η-C_5H_4), 85.3 (*ipso*-η-C_5H_4), 84.1 (η-C_5H_4), 83.7 (η-C_5H_4) and 20.3 ($S_2C_6H_3CH_3$); δ_P ($CDCl_3$) 45.9.

Synthesis of [(PPh$_3$)Ru(μ$_2$-η^5:η^5-C$_{10}$H$_8$)(μ$_2$-S^{t}Bu)$_2$Ru](S^{t}Bu)(BF$_4$) (6a). A solution of **2a** (107 mg, 0.090 mmol) in CH_2Cl_2 (50 ml) was treated with the solution of ^{t}BuSNa prepared from Na (100 mg) and ^{t}BuSH (20 mg) in MeOH (2 ml). The mixture was stirred for 20 h and then the solvent was evaporated under reduced pressure. The residue was chromatographed on silica gel by elution with CH_3CN–Et_2O (1:1) to give **6a** as red crystals (27 mg, 32%), mp >210 °C (Found: C, 50.84; H, 5.22. $C_{40}H_{50}BF_4PRu_2S_3$ requires C, 50.74; H, 5.32%); δ_H ($CDCl_3$) 7.5–7.3 (15H, m, PPh_3), 5.74 (2H, t, η-C_5H_4), 5.32 (2H, t, η-C_5H_4), 4.91 (2H, t, η-C_5H_4), 4.59 (2H, t, η-C_5H_4), 1.35 (18H, s, μ-^{t}BuS) and 0.77 (9H, s, ^{t}BuS$^-$); δ_C ($CDCl_3$) 136.8 (m, *ipso*-Ph), 133.3 (m, *o*-Ph), 130.0 (br, *p*-Ph), 127.2 (m, *m*-Ph), 90.2 (η-C_5H_4), 85.8 (η-C_5H_4), 82.2 (η-C_5H_4), 80.8 (*ipso*-C_5H_4), 79.0 (η-C_5H_4), 48.3 (*ipso*-μ$_2$-^{t}BuS), 44.6 (*ipso*-^{t}BuS$^-$), 32.1 (μ$_2$-^{t}BuS) and 29.2 (^{t}BuS$^-$); δ_P ($CDCl_3$) 28.4.

Crystal structure determinations of 2–6

The X-ray diffraction measurements were performed on a MAC Science Rapid Diffraction Image Processor (DIP 3000) with graphite-monochromated Mo-Kα radiation and an 18-kW rotation-anode generator. Reflections were collected using 30 continuous Weissenberg photographs with a Ψ range of 6°. The unit-cell parameters were determined by autoindexing several images in each data set separately with the DENZO program. Oscillation Images were processed by using the SCALEPACK program. The structure was solved with the DIRDIF-PATTY or SIR method in CRYSTAN-G (software-pack for structure determination) program system and refined finally by the full-matrix least squares procedure. The hydrogen atoms, located from difference Fourier maps or calculation, were isotopically refined.

2b. Single crystals of **2b** were grown from a solution of **2a** in the presence of NH_4PF_6 in CH_3CN by diffusion of diethyl ether vapor at −10 °C for several days. $C_{54}H_{50}F_{12}N_4P_4Ru_2$, M_r = 1309.034, triclinic, space group $P\bar{1}$, a = 9.1510(8), b = 10.180(2), c = 15.852(2) Å, α = 83.319(6), β = 103.008 (7), γ = 104.474(8)°, V = 1390.3(3) Å^3, Z = 1, D_c = 1.563 Mg m^{-3}, μ(Mo-Kα) = 0.739 mm^{-1}, 6024 measured reflections, R = 0.0892 ($I > 2\sigma(I)$, 5731 reflections), GOF = 1.200.

3a·CH_2Cl_2·$C_6H_4(OH)_2$. Single crystals formulated as **3a**·CH_2Cl_2·$C_6H_4(OH)_2$ were grown from the oxidized solution of **2a** with a stoichiometric amount of benzoquinone and BF_3·Et_2O in CH_2Cl_2 and addition of C_6H_5SH at −10 °C for several days. Red needles, $C_{65}H_{56}B_2Cl_2F_8O_2P_2Ru_2S_2$, M_r = 1441.889, monoclinic, space group $P2_1/c$, a = 10.835(1), b = 22.267(4), c = 25.606(4) Å, β = 100.057(7)°, V = 6083.0(2) Å^3, Z = 4, D_c = 1.575 Mg m^{-3}, μ(Mo-Kα) = 0.78 mm^{-1}, 17358 measured reflections, R = 0.065 ($I > 3\sigma(I)$, 4446 reflections), GOF = 1.137. The ^{1}H NMR signals of **3a**·CH_2Cl_2·$C_6H_4(OH)_2$ correspond with those of **3a** except for the signals of $C_6H_4(OH)_2$ and CH_2Cl_2. The atom B(2) was refined isotopically.

4a·CH_2Cl_2. Single crystals formulated as **4a**·CH_2Cl_2 were grown from a solution of **4a** in CH_2Cl_2 by diffusion of diethyl ether vapor at −10 °C. Black red needles, $C_{35}H_{30}Cl_2Ru_2S_4$, M_r = 851.927, monoclinic, space group $P2_1$, a = 10.3140(5), b = 13.4390(8), c = 12.8140(9) Å, β = 102.500(2)°, V = 1734.0(2) Å^3, Z = 2, D_c = 1.632 Mg m^{-3}, μ(Mo-Kα) = 1.290 mm^{-1}, 6517 measured reflections, R = 0.0495 ($I > 2\sigma(I)$, 5763 reflections), GOF = 1.080. The spectral data indicate the single crystal contains one molecule of CH_2Cl_2. In the final Fourier map, two Cl atoms of the CH_2Cl_2 were located as three positions with almost same electron densities and the refined as Cl(1), Cl(2) and Cl(3) with 67% occupancy each.

4c. Single crystals formulated as **4c** were grown from a solution of **4c** in CH_2Cl_2 by diffusion of ether vapor at −10 °C. Black red needles, $C_{34}H_{24}Cl_4Ru_2S_4$, M_r = 904.75, triclinic, space group $P\bar{1}$, a = 7.1130(4), b = 13.2430(10), c = 19.248(2) Å, α = 106.481(4), β = 95.341(6), γ = 99.585(4)°, V = 1695.4(3) Å^3, Z = 2, D_c = 1.772 Mg m^{-3}, μ(Mo-Kα) = 1.478 mm^{-1}, 7631 measured reflections, R = 0.0570 ($I > 2\sigma(I)$, 7176 reflections) GOF = 1.199.

5a·$C_6H_4(OH)_2$. Single crystals formulated as **5a**·$C_6H_4(OH)_2$ were grown from the oxidized solution of **2a** with a stoichiometric amount of benzoquinone and BF_3·Et_2O in CH_2Cl_2 and addition of 1,2-benzenedithiolate at −10 °C for several days. The ^{1}H NMR signals of **5a**·$C_6H_4(OH)_2$ correspond with those of **5a** except for the signals of $C_6H_4(OH)_2$. Orange–red needles, $C_{58}H_{48}B_2F_8O_2P_2Ru_2S_2$, M_r = 1278.842, triclinic, space group $P\bar{1}$, a = 10.5000(5), b = 14.0460(7), c = 20.385(1) Å, α = 94.024(2), β = 97.434(2), γ = 107.514(2)°, V = 2824.0(3) Å^3, Z = 2, D_c = 1.504 Mg m^{-3}, μ(Mo-Kα) = 0.73 mm^{-1}, 10295 measured reflections, R = 0.0811 ($I > 2\sigma(I)$, 7168 reflections), GOF = 1.051. The ^{1}H NMR spectral data indicate the single crystal contains one molecule of $C_6H_4(OH)_2$.

6b. Single crystals formulated as **6b** were grown from a solution of **6a** in CH_3CN containing in large amount of NH_4PF_6 by diffusion of diethyl ether vapor at −10 °C for several days. Red needles, $C_{40}H_{50}F_6P_2Ru_2S_3$, M_r = 1005.108, triclinic, space group $P\bar{1}$, a = 10.8940(9), b = 12.492(1), c = 17.162(2) Å, α = 77.769(3), β = 87.894(4), γ = 72.83(4)°, V = 2180.0(4) Å^3, Z = 2, D_c = 1.531 Mg m^{-3}, μ(Mo-Kα) = 0.96 mm^{-1}, 8775 measured reflections, R = 0.081 ($I > 3\sigma(I)$, 4105 reflections), GOF = 1.294.

CCDC reference numbers 191659–191664 for complexes **2b**, **3a**, **4a**, **4c**, **5b** and **6b**, respectively.

See http://www.rsc.org/suppdata/dt/b2/b207928n/ for crystallographic data in CIF or other electronic format.

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