



Ferrole-type compounds containing thiophenic or thiepinic rings in the 3,4-positions of the metallacycle

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ABSTRACT

The new ferrole $\text{Fe}_2(\text{CO})_6[\mu\text{-}\eta^2, \eta^4\text{-}(\text{Fc})\text{C}=\text{C}(\text{H})=\text{C}(\text{R})\text{S}]\text{C}=\text{C}(\text{SiMe}_3)$ [$\text{R} = \text{SiMe}_3$ (**1**) and $\text{R} = \text{Fc}$ (**2**)] and ruthenoles $\text{Ru}_2(\text{CO})_6[\mu\text{-}\eta^2, \eta^4\text{-}(\text{Me}_3\text{Si})\text{C}=\text{C}(\text{SC}(\text{Fc})=\text{C}(\text{H}))\text{C}=\text{C}(\text{Fc})]$ **3** and $\text{Ru}_2(\text{CO})_6[\mu\text{-}\eta^2, \eta^4\text{-}(\text{Me}_3\text{Si})\text{C}=\text{C}(\text{SC}=\text{CFc})\text{C}(\text{H})=\text{C}(\text{Fc})]$ **4**, have been obtained from the reactions of $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Fe}, \text{Ru}$) and $\text{FcC}=\text{CSC}=\text{CSiMe}_3$ through S–C bond activations and C–C coupling reactions. Thermolysis of $\text{Ru}_2(\text{CO})_6[\mu_3\text{-}\eta^2, \eta^4, \eta^3\text{-}(\text{Me}_3\text{Si})\text{C}=\text{C}(\text{SC}(\text{Fc})=\text{C}(\text{SC}=\text{CSiMe}_3)\text{Ru}(\text{CO})_3)\text{C}=\text{C}(\text{Fc})]$ alone and in the presence of $\text{HC}\equiv\text{CFc}$, yielded the compounds $\text{Ru}_2(\text{CO})_6[\mu\text{-}\eta^2, \eta^4\text{-}(\text{Me}_3\text{Si})\text{C}=\text{C}(\text{SC}(\text{Fc})=\text{C}(\text{SC}=\text{CSiMe}_3))\text{C}=\text{C}(\text{Fc})]$ **5** and $\text{Ru}_2(\text{CO})_6[\mu\text{-}\eta^2, \eta^4\text{-}(\text{Me}_3\text{Si})\text{C}=\text{C}(\text{SC}(\text{Fc})=\text{C}(\text{SC}=\text{CSiMe}_3)\text{C}(\text{H})=\text{C}(\text{Fc}))\text{C}=\text{C}(\text{Fc})]$ **6**, respectively. The crystal structures of the compounds **1**, **3**, **4** and **6** are reported.

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1. Introduction

Studies on reactivity of acetylenes in the presence of transition metals have attracted research interest since the organic synthesis point of view. Metal carbonyls of the iron triad react with alkynes to afford “ferrole-type” species such as $\text{Fe}_2(\text{CO})_6[(\text{CH}_3\text{OCH}_2)\text{C}=\text{C}(\text{H})\text{C}(\text{H})=\text{C}(\text{CH}_2\text{OCH}_3)]$ [**1**], $\text{Fe}_2(\text{CO})_6[(\text{R})\text{C}=\text{C}(\text{H})-\text{C}(\text{H})=\text{C}(\text{R})]$ ($\text{R} = 17\alpha\text{-estradiol}$) [**2**], ($\text{R} = \text{Fc}$) [**3**], $\text{Fe}_2(\text{CO})_6[(\text{CH}_3\text{COO})\text{C}=\text{C}(\text{Ph})\text{C}(\text{Ph})=\text{C}(\text{OOCCH}_3)]$ [**4**], $\text{Fe}_2(\text{CO})_6[\text{C}_4(\text{SMe})_4]$ [**5**], $\text{Ru}_2(\text{CO})_6\{\text{CH}_3(\text{H}_2\text{C}=\text{C})\text{C}=\text{C}(\text{Et})\text{C}(\text{=CH}_2)\text{CH}_3\}=\text{C}(\text{Et})$ [**6**], $[\text{Os}_2(\text{CO})_6-(\text{C}_4\text{H}_4)]$ [**7**]. Also, the diynes $\text{RC}\equiv\text{C}-\text{C}\equiv\text{R}$ ($\text{R} = \text{Ph}, \text{Fc}$) and the poly-yne $\text{Me}_3\text{SiC}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3$ use only one of their carbon–carbon triple bonds to give the complexes $\text{Ru}_2\text{CO}_6[\mu\text{-}\eta^2, \eta^4\text{-}(\text{Ph})\text{C}=\text{C}(\text{C}\equiv\text{CPh})\text{C}(\text{PhC}\equiv\text{C})=\text{C}(\text{Ph})]$ [**8**], $\text{Os}_2\text{CO}_6[\mu\text{-}\eta^2, \eta^4\text{-}(\text{FcC}\equiv\text{C})-\text{C}=\text{C}(\text{Fc})\text{C}(\text{Fc})=\text{C}(\text{C}\equiv\text{CFc})]$ [**9**], $\text{Ru}_2\text{CO}_6[\mu\text{-}\eta^2, \eta^4\text{-}(\text{Me}_3\text{SiC}\equiv\text{C})\text{C}=\text{C}(\text{C}\equiv\text{CSiMe}_3)\text{C}(\text{C}\equiv\text{CSiMe}_3)=\text{C}(\text{C}\equiv\text{CSiMe}_3)]$ [**10**] and $\text{Ru}_2(\text{CO})_6-[\text{C}_4\text{Fc}_2(\text{C}\equiv\text{CFc})_2]$ [**11**]. Some ferrole-type compounds have been reported to act as intermediates in synthesis of organic products [**4,12**].

To our knowledge, the number of ruthenole derivatives described is scarce compared to the widely developed chemistry of ferrole compounds. This fact seems to indicate that the formation of the latter derivatives is more favored than the analogous

ruthenoles. Thus, the alkylalkynyl thioethers $\text{EtSC}\equiv\text{CR}$ ($\text{R} = \text{Me}, \text{Ph}$) which behave as alkynes bearing the thiolate SET as substituent, yield the ferroles $[\text{Fe}_2(\text{CO})_6\{\text{C}(\text{Ph})\text{C}(\text{SEt})\text{C}(\text{SEt})\text{C}(\text{Ph})\}]$ [**13**], $[\text{Fe}_2(\text{CO})_6\{\text{C}(\text{SEt})\text{C}(\text{R})\text{C}(\text{R})\text{C}(\text{SEt})\}]$ ($\text{R} = \text{Me}, \text{Ph}$) [**14**] and $[\text{Fe}_2(\text{CO})_6\{\text{C}(\text{R})\text{C}(\text{SEt})\text{C}(\text{R})\text{C}(\text{SEt})\}]$ ($\text{R} = \text{Me}, \text{Ph}$) [**14**] in their reactions with iron carbonyls while ruthenole derivatives are not obtained using ruthenium carbonyls instead.

On the other hand, compounds of the ferrole-type family, containing sulfur substituents in the metallacycle, are not common. Among them, we have previously reported the ruthenole $\text{Ru}_2(\text{CO})_6[\mu_3\text{-}\eta^2, \eta^4\text{-}(\text{Fc})\text{C}=\text{C}\{\text{SC}(\text{Fc})\text{C}(\text{SC}=\text{CFc})\text{CO}\}\text{C}=\text{C}(\text{Fc})]$ [**15**] which bears a thiopyranone ring. These results prompted us to prepare new ferrole-type compounds containing sulfur substituents with a view to probing their ability to act as intermediates in the synthesis of organosulfur derivatives.

The synthesis and characterization of a series of ferrole and ruthenole compounds containing organosulfur substituents in the metallacyclopentadienyl ring are described here. The crystal structures of compounds **1**, **3**, **4** and **6** have been solved by X-ray diffraction methods

2. Results and discussion

The new compounds $\text{Fe}_2(\text{CO})_6[\mu\text{-}\eta^2, \eta^4\text{-}(\text{Fc})\text{C}=\text{C}\{\text{C}(\text{H})=\text{C}(\text{R})\text{S}\}-\text{C}=\text{C}(\text{SiMe}_3)]$ [$\text{R} = \text{SiMe}_3$ (**1**) and $\text{R} = \text{Fc}$ (**2**)] (Scheme 1) the earlier

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reported derivatives $[\text{Fe}_2(\text{CO})_6(\mu\text{-SC}=\text{C}(\text{H})\text{SiMe}_3)]$ [16] and $[\text{Fe}_2(\text{CO})_6(\mu\text{-}\eta^2, \eta^4\text{-Fc})\text{C}=\text{C}(\text{H})\text{C}(\text{H})=\text{C}(\text{Fc})]$ [3] were obtained from the reaction of $\text{Fe}_3(\text{CO})_{12}$ and $\text{FcC}=\text{CSC}=\text{CSiMe}_3$ in CH_2Cl_2 at 45°C after chromatographic workup. Also, the analogous ruthenoles $\text{Ru}_2(\text{CO})_6[\mu\text{-}\eta^2, \eta^4\text{-(Me}_3\text{Si)C}=\text{C}\{\text{SC}(\text{Fc})=\text{C}(\text{H})\}\text{C}=\text{C}(\text{Fc})]$ **3** and $\text{Ru}_2(\text{CO})_6[\mu\text{-}\eta^2, \eta^4\text{-(Me}_3\text{Si)C}=\text{C}(\text{SC}=\text{CFc})\text{C}(\text{H})=\text{C}(\text{Fc})]$ **4** (Scheme 1), together with the known compounds $[\text{Ru}_3(\text{CO})_9(\mu\text{-}\eta^1\text{-SC}=\text{CFc})(\mu^3\text{-}\eta^2\text{-C}=\text{CSiMe}_3)]$ [17], $\text{Ru}_2(\text{CO})_6[\mu_3\text{-}\eta^2, \eta^4, \eta^3\text{-(Me}_3\text{Si)C}=\text{C}\{\text{SC}(\text{Fc})=\text{C}(\text{H})\}\text{C}=\text{C}(\text{Fc})]$ [17], and $[\text{Ru}_2(\text{CO})_6(\mu\text{-}\eta^1\text{-SC}=\text{CSiMe}_3)(\mu\text{-}\eta^2\text{-C}=\text{CFc})]$ [17] were synthesized by a similar reaction between $\text{Ru}_3(\text{CO})_{12}$ and $\text{FcC}=\text{CSC}=\text{CSiMe}_3$ in toluene at 65°C .

The IR spectra in the CO area exhibit the characteristic ν_{CO} bands for hexacarbonyldimetal derivatives [18]. Additionally, compound $\text{Ru}_2(\text{CO})_6[\mu\text{-}\eta^2, \eta^4\text{-(Me}_3\text{Si)C}=\text{C}(\text{SC}=\text{CFc})\text{C}(\text{H})=\text{C}(\text{Fc})]$ **4**, shows a very weak $\nu_{\text{C}=\text{C}}$ band at 2153 cm^{-1} for the $\text{SC}=\text{CFc}$ group. In the ^1H NMR spectra, resonances assignable to the Fc, SiMe₃ groups and the olefinic protons are observed and the peaks corresponding to the molecular ion are showed in the FAB-MS spectra of all compounds.

The crystal structure of $\text{Fe}_2(\text{CO})_6[\mu\text{-}\eta^2, \eta^4\text{-(Fc)C}=\text{C}\{\text{C}(\text{H})=\text{C}(\text{SiMe}_3)\text{S}\}\text{C}=\text{C}(\text{SiMe}_3)]$ **1** (Fig. 1), $\text{Ru}_2(\text{CO})_6[\mu\text{-}\eta^2, \eta^4\text{-(Me}_3\text{Si)C}=\text{C}\{\text{SC}(\text{Fc})=\text{C}(\text{H})\}\text{C}=\text{C}(\text{Fc})]$ **3**, (Fig. 2) and $\text{Ru}_2(\text{CO})_6[\mu\text{-}\eta^2, \eta^4\text{-(Me}_3\text{Si)C}=\text{C}(\text{SC}=\text{CFc})\text{C}(\text{H})=\text{C}(\text{Fc})]$ **4** (Fig. 3) have been confirmed by an X-ray diffraction study.

In compounds $\text{Fe}_2(\text{CO})_6[\mu\text{-}\eta^2, \eta^4\text{-(Fc)C}=\text{C}\{\text{C}(\text{H})=\text{C}(\text{R})\text{S}\}\text{C}=\text{C}(\text{SiMe}_3)]$ [R = SiMe₃ (**1**), R = Fc (**2**)] and $\text{Ru}_2(\text{CO})_6[\mu\text{-}\eta^2, \eta^4\text{-(Me}_3\text{Si)C}=\text{C}\{\text{SC}(\text{Fc})=\text{C}(\text{H})\}\text{C}=\text{C}(\text{Fc})]$ **3**, the molecule consists of a “ferrole-type” structure containing either a 2-trimethylsilyl- or 2-ferrocenyl-thiophenic substituent located fused to C(3, 4) of the metallacyclopentadienyl ring. It seems that the formation of these compounds takes place through a head to head C–C coupling between the $\text{C}=\text{CR}$ and $\text{SC}=\text{R}'$ fragments, generated by rupture of a C–S bond in the thioether, affording a thiolate, which is coupled with a molecule of alkyne $\text{HC}=\text{CR}$ (R = SiMe₃ or Fc) to close the ring. This alkyne is formed by protonation of the $\text{C}=\text{CR}$ fragment as a consequence of some moisture in the solvent.

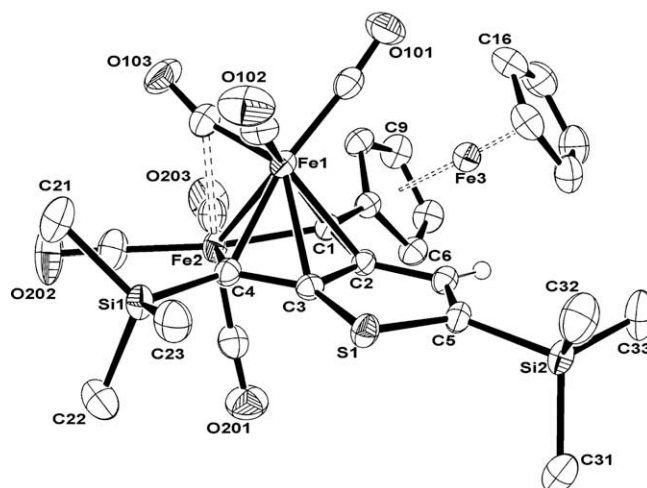
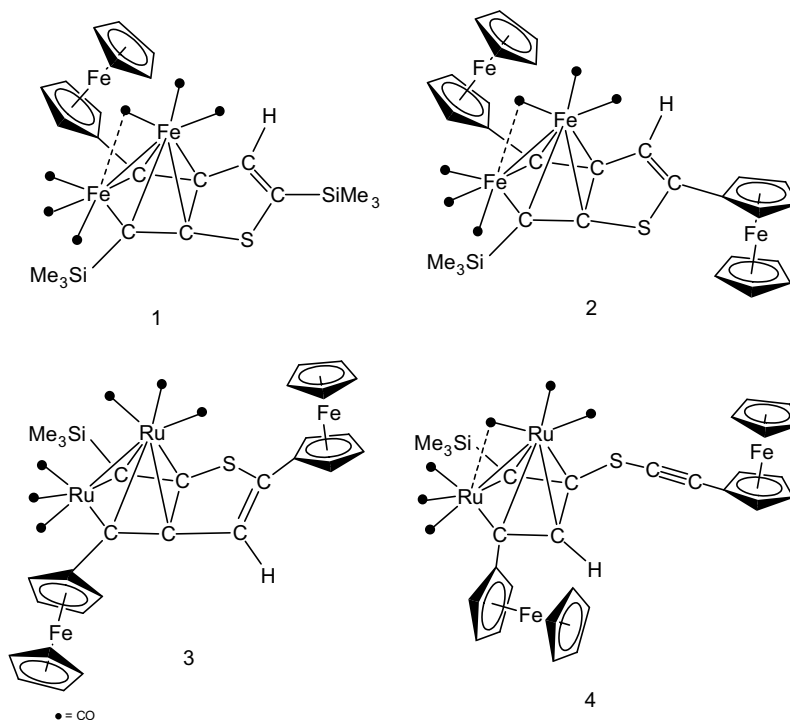


Fig. 1. Molecular structure of **1**. The thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles ($^\circ$): Fe(2)–C(1) 2.039(2); Fe(2)–C(4) 2.058(2); C(1)–C(2) 1.436(3); C(2)–C(3) 1.453(3); C(3)–C(4) 1.427(3); C(3)–S(1) 1.774(2); C(2)–C(6) 1.458(3); C(5)–S(1) 1.768(2); C(5)–C(6) 1.375(3); Fe(1)–Fe(2) 2.506(1); Fe(1)–C(103) 1.826(3); Fe(2)–C(103) 2.352(2); Fe(1)–C(103)–O(103) 161.0(2).

Further coordination of the new organic ligands to the $\text{M}_2(\text{CO})_6$ (M = Fe, Ru) units yields the compounds **1–3**. Similar rupture of a S–C bond and coupling between $\text{C}=\text{CR}$ groups have been described in the reaction of the alkylalkynyl thioethers $\text{EtSC}=\text{CR}$ (R = Me, Ph) with $\text{Fe}_3(\text{CO})_{12}$ in refluxing hexane, although the trinuclear clusters $[\text{Fe}_3(\text{CO})_8\{\mu_3\text{-(SEt)C}=\text{C}(\text{R})\text{C}(\text{R})=\text{C}\}(\mu\text{-SEt})]$ and $[\text{Fe}_3(\text{CO})_8\{\mu_3\text{-(R)C}=\text{C}(\text{SEt)C}(\text{R})=\text{C}\}(\mu\text{-SEt})]$ (R = Me or Ph) [14] which contain a bridging thiolate ligand and a ferrole unit in the molecule have been obtained instead of dinuclear species.

In contrast, compound $\text{Ru}_2(\text{CO})_6[\mu\text{-}\eta^2, \eta^4\text{-(Me}_3\text{Si)C}=\text{C}(\text{SC}=\text{CFc})\text{C}(\text{H})=\text{C}(\text{Fc})]$ **4** is formed by a C–C coupling reaction between one of the $\text{C}=\text{C}$ triple bond in the thioether $\text{FcC}=\text{CSC}=\text{CSiMe}_3$



Scheme 1. Formula of compounds **1–4**.

and a molecule of the alkyne $\text{HC}\equiv\text{Cfc}$. In this case, cleavage of the S–C bond does not occur and, as we mentioned before, examples are reported of diynes or poly-ynes which use only one of the $\text{C}\equiv\text{C}$ triple bond to yield ferrole-type derivatives [8–11].

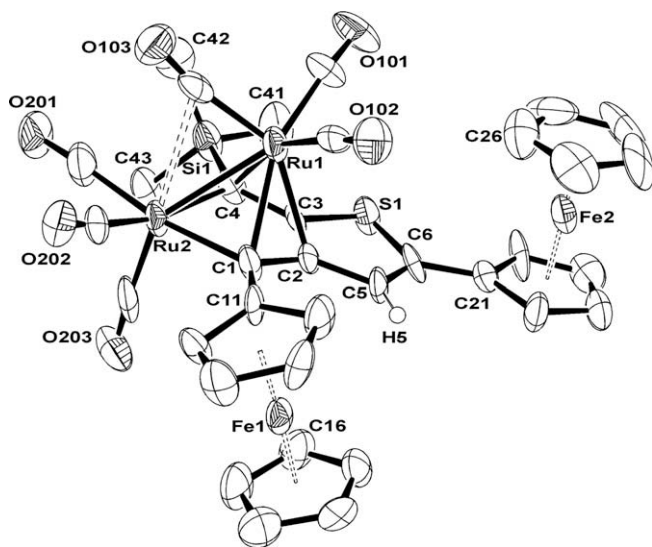


Fig. 2. Molecular structure of **3**. The thermal ellipsoids are drawn at the 50% probability level.

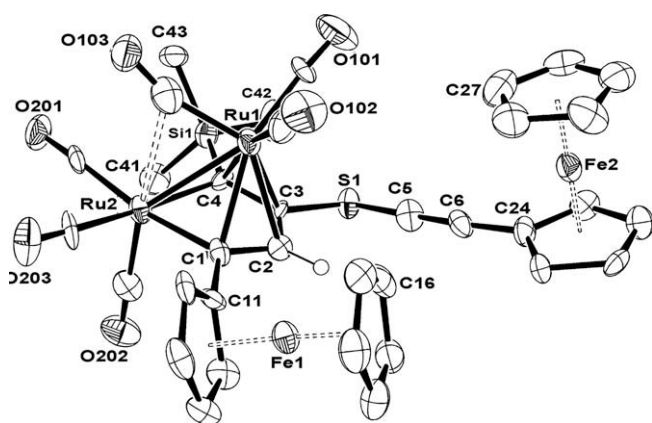
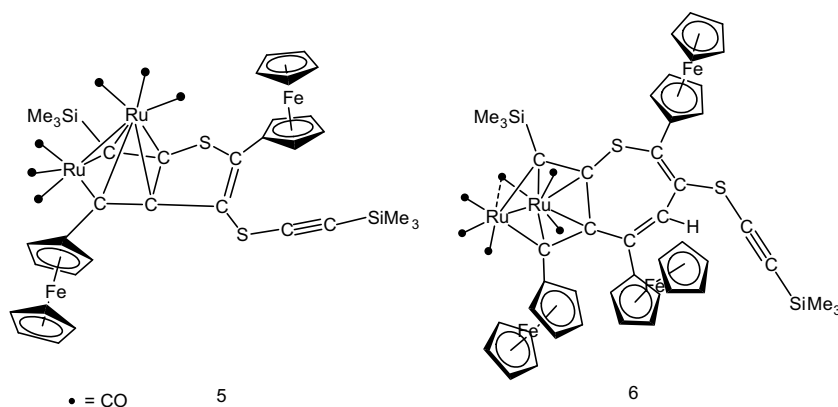


Fig. 3. Molecular structure of **4**. The thermal ellipsoids are drawn at the 50% probability level.



Scheme 2. Formula of compounds **5**–**6**.

The known compound $\text{Fe}_2(\text{CO})_6[\mu\text{-}\eta^2, \eta^4\text{-}(\text{Fc})\text{C}=\text{C}(\text{H})\text{C}(\text{H})=\text{C}(\text{Fc})]$ [3] was also obtained from the reaction of $\text{Fe}_3(\text{CO})_{12}$ and $\text{FcC}\equiv\text{CSC}\equiv\text{CSiMe}_3$. However, the fact that the spectroscopic data reported for it [ν_{CO} (2020 vs, 1971 vs, 1896 s, br, 1777 m) and ^1H NMR resonances $\{\delta$ 4.93 (s, 2H, $\text{HC}=\text{C}$), 4.28–4.48 (m, 8H, C_5H_4), 4.17 (s, 10H, C_5H_5)] were different than those found by us [ν_{CO} (2064 m, 2030 vs, 1996 s, 1982 m, 1942 w) and the ^1H NMR $\{\delta$ 6.48 (s, 2H, $\text{HC}=\text{C}$), 4.38 (m, 2H, C_5H_4), 4.31 (m, 4H, C_5H_4), 4.28 (m, 2H, C_5H_4), 4.19 (s, 10H, C_5H_5)]}, prompted us initially to believe that the $\text{Fe}_2(\text{CO})_6[\mu\text{-}\eta^2, \eta^4\text{-}(\text{H})\text{C}=\text{C}(\text{Fc})\text{C}(\text{Fc})=\text{C}(\text{H})]$ isomer had been prepared. An X-ray diffraction study carried out on it afforded identical crystal structure that the earlier reported [3] for the compound $\text{Fe}_2(\text{CO})_6[\mu\text{-}\eta^2, \eta^4\text{-}(\text{Fc})\text{C}=\text{C}(\text{H})\text{C}(\text{H})=\text{C}(\text{Fc})]$. Once again, the IR and NMR data of this compound, obtained using crystals from the same crop than the selected one to solve the structure, were coincident with our earlier results.

Compound $\text{Ru}_2(\text{CO})_6[\mu\text{-}\eta^2, \eta^4\text{-}(\text{Me}_3\text{Si})\text{C}=\text{C}(\text{SC}(\text{Fc})=\text{C}(\text{SC}\equiv\text{CSiMe}_3))\text{C}=\text{C}(\text{Fc})]$ **5** has been prepared by heating a toluene solution of $\text{Ru}_2(\text{CO})_6[\mu_3\text{-}\eta^2, \eta^4, \eta^3\text{-}(\text{Me}_3\text{Si})\text{C}=\text{C}(\text{SC}(\text{Fc})=\text{C}(\text{SC}\equiv\text{CSiMe}_3)\text{-Ru}(\text{CO})_3)\text{C}=\text{C}(\text{Fc})]$ [17] while the same reaction carried out in the presence of $\text{HC}\equiv\text{Cfc}$ yielded the compound $\text{Ru}_2(\text{CO})_6[\mu\text{-}\eta^2, \eta^4\text{-}(\text{Me}_3\text{Si})\text{C}=\text{C}(\text{SC}(\text{Fc})=\text{C}(\text{SC}\equiv\text{CSiMe}_3)\text{C}(\text{H})=\text{C}(\text{Fc}))\text{C}=\text{C}(\text{Fc})]$ **6** together with the organic compound 1,2,4- $\text{C}_6\text{H}_3(\text{Fc})_3$ (Scheme 2).

The IR spectra in the CO region of compounds **5** and **6** display a weak broad $\nu_{\text{C}=\text{C}}$ band and the expected pattern for “ferrole-type” compounds [18] that are similar to those observed in compounds **1**–**4**. Resonances corresponding to the ferrocenyl and trimethylsilyl groups are also present in their ^1H NMR spectra. Additionally, a signal that appears at 6.99 ppm in the ^1H NMR spectrum of compound **6** was assigned to the olefinic proton of the thienepinic ring. The FAB- and MALDI-MS for the compounds $\text{Ru}_2(\text{CO})_6[\mu\text{-}\eta^2, \eta^4\text{-}(\text{Me}_3\text{Si})\text{C}=\text{C}(\text{SC}(\text{Fc})=\text{C}(\text{SC}\equiv\text{CSiMe}_3))\text{C}=\text{C}(\text{Fc})]$ **5** and $\text{Ru}_2(\text{CO})_6[\mu\text{-}\eta^2, \eta^4\text{-}(\text{Me}_3\text{Si})\text{C}=\text{C}(\text{SC}(\text{Fc})=\text{C}(\text{SC}\equiv\text{CSiMe}_3)\text{C}(\text{H})=\text{C}(\text{Fc}))\text{C}=\text{C}(\text{Fc})]$ **6**, respectively, exhibit peaks corresponding to the molecular ion [m/z 1048 for compound **5** and m/z 1258 for compound **6**] as well as those of the loss of 6 COs. Compound $\text{Ru}_2(\text{CO})_6[\mu\text{-}\eta^2, \eta^4\text{-}(\text{Me}_3\text{Si})\text{C}=\text{C}(\text{SC}(\text{Fc})=\text{C}(\text{SC}\equiv\text{CSiMe}_3))\text{C}=\text{C}(\text{Fc})]$ **5** is formed from the complex $\text{Ru}_2(\text{CO})_6[\mu_3\text{-}\eta^2, \eta^4, \eta^3\text{-}(\text{Me}_3\text{Si})\text{C}=\text{C}(\text{SC}(\text{Fc})\text{C}(\text{SC}\equiv\text{CSiMe}_3)\text{Ru}(\text{CO})_3)\text{C}=\text{C}(\text{Fc})]$ by loss of a $\text{Ru}(\text{CO})_3$ fragment, followed by a C–C coupling reaction between the two carbon atoms linked to this carbonyl fragment, without inclusion of a CO between them, as occurs in the formation of the complex $\text{Ru}_2(\text{CO})_6[\mu_3\text{-}\eta^2, \eta^4\text{-}(\text{Fc})\text{C}=\text{C}(\text{SC}(\text{Fc})\text{C}(\text{SC}\equiv\text{CFc})\text{CO})\text{C}=\text{C}(\text{Fc})]$ [15]. In contrast, substitution of this ruthenium carbonyl fragment by a $\text{HC}\equiv\text{Cfc}$ molecule yields compound $\text{Ru}_2(\text{CO})_6[\mu\text{-}\eta^2, \eta^4\text{-}(\text{Me}_3\text{Si})\text{C}=\text{C}(\text{SC}(\text{Fc})=\text{C}(\text{SC}\equiv\text{CSiMe}_3)\text{C}(\text{H})=\text{C}(\text{Fc}))\text{C}=\text{C}(\text{Fc})]$ **6** which contains a thienepinic ring in the 3,4-positions of the metallacycle of the ruthenole unit instead of a thiophenic ring as shown by the compound **5**. The molecular structure of **6** is depicted in Fig. 4.

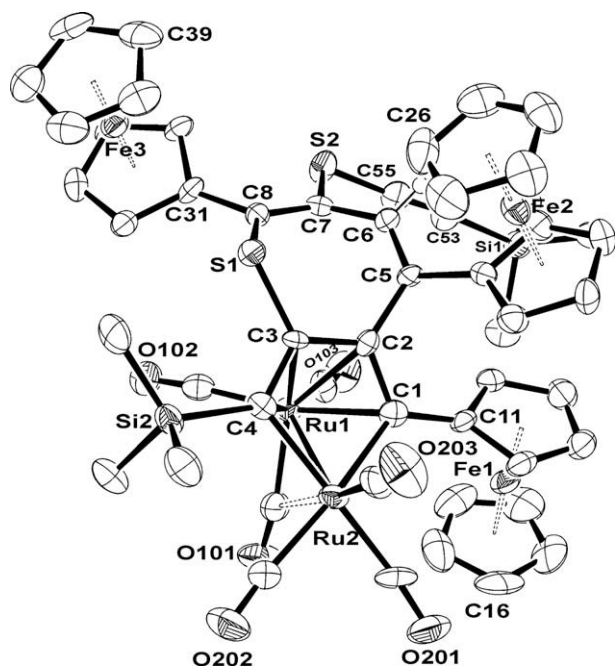


Fig. 4. Molecular structure of **6**. The thermal ellipsoids are drawn at the 50% probability level.

Table 1
Selected bond distances (Å) and angles (°) for compounds **3**, **4** and **6**.

| | 3 | 4 | 6 |
|----------------------------------|-----------|-----------|-----------|
| Ru(2)–C(1) | 2.152(11) | 2.101(8) | 2.133(7) |
| Ru(2)–C(4) | 2.166(11) | 2.168(9) | 2.142(7) |
| C(1)–C(2) | 1.450(15) | 1.406(11) | 1.435(10) |
| C(2)–C(3) | 1.441(15) | 1.419(12) | 1.439(9) |
| C(3)–C(4) | 1.444(15) | 1.420(10) | 1.420(9) |
| C(3)–S(1) | 1.786(11) | 1.816(9) | 1.813(7) |
| Ru(1)–Ru(2) | 2.713(2) | 2.729(2) | 2.748(2) |
| Ru(2)–C(10x) ^a | 2.805(14) | 2.622(11) | 2.672(8) |
| Ru(1)–C(10x) ^a | 1.936(15) | 1.894(11) | 1.936(9) |
| Ru(1)–C(10x)–O(10x) ^a | 170.1(11) | 162.6(8) | 163.8(7) |

^a **3** x = 3, **4** x = 3, **6** x = 1

Additionally, the formation of compound 1,2,4-C₆H₃(Fc)₃ in this reaction, was confirmed by ¹H NMR data. A few fears ago, it was reported [19] the photolysis of a hexane solution of Ru(CO)₅ and HC≡CFC under a CO atmosphere as a way to obtain it. We suppose that in our case, the Ru(CO)₃ fragment which is eliminated from the starting compound Ru₂(CO)₆[μ₃-η²,η⁴,η³-(Me₃Si)-C≡C{SC(Fc)=C(SC≡CSiMe₃)Ru(CO)₃}C=C(SiMe₃)] to afford compound **6**, acts as a catalyst in the [2+2+2] cycloaddition of the alkyne HC≡CFC to yield the derivative 1,2,4-C₆H₃(Fc)₃.

Studies on the ability of these compounds to act as intermediates in the synthesis of new organosulfur derivatives are in progress and will be published elsewhere. At the moment we found, on the basis of IR and H NMR spectroscopy together with mass spectrometry data that the new compound 2,4-bis(ferrocenyl)-6-(trimethylsilyl)cyclopentathiophen-5-one seems to be generated in the reaction of compound **2** and S₈ in toluene at 80 °C. Additional results obtained from other reactions are not conclusive yet.

3. Crystal structures

Single crystal X-ray studies have confirmed that compounds **1**, **3**, **4** and **6** exhibit a “ferrole-type” structure. Although crystallographic data corresponding to several ferrole compounds have

been described, to our knowledge, only a few crystal structures of ruthenoles have been determined. Selected bond distances and angles for compound Fe₂(CO)₆[μ-η²,η⁴-(Fc)C≡C{C(H)=C(SiMe₃)S}C=C(SiMe₃)] **1** are collected as Fig. 1 caption while for compounds Ru₂(CO)₆[μ-η²,η⁴-(Me₃Si)C≡C{SC(Fc)=C(H)}C=C(Fc)] **3**, Ru₂(CO)₆[μ-η²,η⁴-(Me₃Si)C≡C{SC(Fc)=C(SC≡CSiMe₃)C(H)=C(Fc)}C=C(Fc)] **4** and Ru₂(CO)₆[μ-η²,η⁴-(Me₃Si)C≡C{SC(Fc)=C(SC≡CSiMe₃)C(H)=C(Fc)}C=C(Fc)] **6** are listed in Table 1.

The C(1)–C(2), C(2)–C(3) and C(3)–C(4) distances in the metallacycle of compounds **1** [1.436(3), 1.453(3) and 1.427(3) Å], **3** [1.450(15), 1.441(15) and 1.444(15) Å], **4** [1.406(11), 1.419(12) and 1.420(10) Å] and **6** [1.435(10), 1.439(9) and 1.420(9) Å] are in the expected range for this type of compounds Fe₂(CO)₆[C₂Et₂C(CH₂N(Me)CH₂Ph)CH] [20], Fe₂(CO)₆[C₄(SMe₄)] [5], Fe₂(CO)₆[C(OCOPh)C(OMe)C(H)C(H)] [21], Ru₂(CO)₆[μ-η²,η⁴-C(C≡CPh)=CPhC(C≡CPh)=CPh] [18c], Ru₂(CO)₆[μ-η²,η⁴-(Fc)C≡C(H)C(H)=C(Fc)] [18a], Ru₂(CO)₆[μ-η²,η⁴-C₄(CO₂Me)₄] [22], Ru₂(CO)₆[μ-η²,η⁴-C₄(CH₂OH)₄] [23], Ru₂(CO)₆[μ-η²,η⁴-(MeCO₂)C≡C(CH₂OCH₂)C=C(CO₂Me)] [12d], [Ru₂(CO)₆(μ-η²,η⁴-C₁₀H₆C₄Ph₂)] [24].

Two conformers have been theoretically predicted for this type of compounds [25]. The “sawhorse” isomer shows an eclipsed arrangement of the carbonyls while in the “non-sawhorse” isomer the COs are staggered, one of the carbonyls being semibridging.

The Fe(1)–C(103) and Fe(2)–C(103) distances [1.826(3) and 2.352(2) Å, respectively, for compound **1**] Ru(1)–C(103) and Ru(2)–C(103) [1.936(15) and 2.805(14) Å, respectively, for compound **3**], Ru(1)–C(103) and Ru(2)–C(103) [1.894(11) and 2.622(11) Å, respectively, for compound **4**] and Ru(1)–C(101) and Ru(2)–C(101) [1.936(9) and 2.672(8) Å, respectively, for compound **6**] are indicative that this CO acts as a semibridging ligand between both metal atoms. This fact, also confirmed by a weak band that appears in the IR spectra of compounds **1**, **2**, **4** and **6**, agrees with a “non-sawhorse” geometry for these compounds.

Values of 2.506(1) [Fe(1)–Fe(2)] as well as 2.713(2), 2.729(2) and 2.748(2) [Ru(1)–Ru(2)] Å found in the compounds **1**, **3**, **4** and **6**, respectively, are similar to those observed in the above mentioned compounds and other diiron or diruthenium derivatives.

4. Conclusions

The compounds **1–3** have been formed by rupture of one S–C bond in FcC≡CSC≡CSiMe₃ in the presence of iron and ruthenium carbonyls together with C–C coupling reactions between different groups containing carbon–carbon triple bonds, while compound **4** seems to be generated by coupling of one of the C≡C triple bonds in FcC≡CSC≡CSiMe₃ and a HC≡CFC molecule.

Thermolytic elimination of the fragment Ru(CO)₃ from the trinuclear compound Ru₂(CO)₆[μ₃-η²,η⁴,η³-(Me₃Si)C≡C{SC(Fc)=C(SC≡CSiMe₃)Ru(CO)₃}C=C(Fc)] affords the new ruthenole **5** which contains a thiophenic substituent in the metallacycle while an analogous reaction carried out in the presence of the alkyne HC≡CFC yields the ruthenole **6** bearing a thiepinic ring.

X-ray diffraction studies confirmed a “non-sawhorse” geometry for the compounds **1**, **3**, **4** and **6**.

5. Experimental

5.1. General procedures

All reactions were carried out under argon atmosphere. Solvents were dried using standard methods. IR spectra were recorded on a Perkin–Elmer Spectrum BX FT-IR spectrophotometer using NaCl cells. ¹H NMR spectra were registered on a Bruker AMX-300 instrument. Elemental analyses were performed on a Perkin–Elmer 240-B microanalyzer. FAB or MALDI mass spectra

were carried out on a WG Autospec Spectrometer or a 4700 Proteomics Analyzer (Applied Biosystems) using 3-nitrobenzyl alcohol or ditranol as matrix, respectively. $C_5H_5FeC_5H_4C\equiv CSC\equiv CSiMe_3$ [17] was prepared according to published procedures.

5.2. Reaction of $Fe_3(CO)_{12}$ with $C_5H_5FeC_5H_4C\equiv CSC\equiv CSiMe_3$

A mixture of $Fe_3(CO)_{12}$ (200 mg, 0.4 mmol) and $C_5H_5FeC_5H_4C\equiv CSC\equiv CSiMe_3$ (350 mg, 1.0 mmol) in dichloromethane (20 mL) was stirred under argon atmosphere at 45 °C for 22 h. The color of the reaction changed from dark green to dark brown. The solvent was removed under vacuum and the residue was purified by column chromatography. Elution with hexane gave the known compound $[Fe_2(CO)_6\{\mu-\eta^1, \eta^2-SC=C(H)SiMe_3\}]$ [16] (19 mg, 0.045 mmol, 12%). A second brown band eluted with hexane-toluene (10:1) gave compound $Fe_2(CO)_6[\mu-\eta^2, \eta^4-(Fc)C=C\{C(H)=C(SiMe_3)S\}C=C(SiMe_3)]$ **1** (18 mg, 0.025 mmol, 6%). Further elution with hexane-toluene (5:1) afforded an orange band as a mixture of compounds which was repurified by TLC using hexane-toluene (2:1) as eluent, to give a first dark orange band corresponding to known compound $[Fe_2(CO)_6\{\mu-\eta^2, \eta^4-(Fc)C=C(H)C(H)=C(Fc)\}]$ [3] (13 mg, 0.018 mmol, 5%) followed by an orange band of compound $Fe_2(CO)_6[\mu-\eta^2, \eta^4-(Fc)C=C\{C(H)=C(Fc)S\}C=C(SiMe_3)]$ **2** (8 mg, 0.009 mmol, 1%). Single crystals of compound **1** were obtained from hexane at -20 °C. Spectral data for **1**: IR (hexane) cm^{-1} ν_{CO} : 2081 s, 2046 vs, 2015 s, 2010 s, 1967 w. 1H NMR ($CDCl_3$, 300 MHz, 22 °C) δ : 7.91 (s, 1H, HC=C), 4.45 (t, 2H, $J = 1.9$ Hz, C_5H_4), 4.26 (t, 2H, $J = 1.9$ Hz, C_5H_4), 4.19 (s, 5H, C_5H_5), 0.47 (s, 9H, SiMe₃), 0.12 (s, 9H, SiMe₃). MS (FAB⁺) m/z : 716 [M⁺]. Spectral data for **2** IR (hexane) cm^{-1} ν_{CO} : 2058 s, 2021 vs, 1993 s, 1984 m, 1922 w. 1H NMR ($CDCl_3$, 300 MHz, 22 °C) δ : 7.75 (s, 1H, HC=C), 4.74 (m, 1H, C_5H_4), 4.68 (m, 1H, C_5H_4), 4.47 (m, 2H, C_5H_4), 4.37 (m, 3H, C_5H_4), 4.29 (m, 1H, C_5H_4), 4.27 (s, 5H, C_5H_5), 4.19 (s, 5H, C_5H_5), 0.43 (s, 9H, SiMe₃). MS (FAB⁺) m/z : 828 [M⁺], 744–660 [M⁺-nCO; $n = 3-6$]. Anal. Calc. for $C_{35}H_{28}Fe_4SiO_6S$: C, 50.77; H, 3.38; S, 3.86. Found: C, 50.27; H, 3.62; S, 3.86%.

5.3. Reaction of $Ru_3(CO)_{12}$ with $C_5H_5FeC_5H_4C\equiv CSC\equiv CSiMe_3$

A toluene solution (40 mL) of $Ru_3(CO)_{12}$ (400 g, 0.62 mmol) and the thioether $FcC\equiv CSC\equiv CSiMe_3$ (600 mg, 1.78 mmol) was heated at 65 °C for 3 h. The solvent was removed under vacuum and the residue purified by TLC using a mixture of hexane/toluene (10:1.5). Several bands were separated from the chromatography, being the first ones those corresponding to the before reported compounds $[Ru_2(CO)_6\{\mu-\eta^1-SC\equiv CSiMe_3\}(\mu-\eta^2-C\equiv CFc)]$ [17] (traces), $[Ru_3(CO)_9\{\mu-\eta^1-SC\equiv CFc\}(\mu_3-\eta^2-C\equiv CSiMe_3)]$ [17] (60 mg, 0.09 mmol, 15%), $Ru_2(CO)_6[\mu_3-\eta^2, \eta^4, \eta^3-(Me_3Si)C=C\{SC(Fc)=C(SC\equiv CSiMe_3)Ru(CO)_3\}C=C(Fc)]$ [17] (350 mg, 0.29 mmol, 46%), followed by an orange-red band containing a mixture of compounds. This band was treated with cool hexane to separate the compound $Ru_2(CO)_6[\mu-\eta^2, \eta^4-(Me_3Si)C=C\{SC(Fc)=C(H)\}C=C(Fc)]$ **3**, (60 mg, 0.07 mmol, 11%) as soluble fraction, leaving the compound $Ru_2(CO)_6[\mu-\eta^2, \eta^4-(Me_3Si)C=C\{SC\equiv CFc\}C(H)=C(Fc)]$ **4**, (30 mg, 0.03 mmol, 5%). Suitable crystals for X-ray diffraction of the compounds **3** and **4** were obtained in hexane and toluene at -20 °C, respectively. Spectral data for **3**: IR (hexane) cm^{-1} ν_{CO} : 2074 s, 2033 s, 1998 vs, 1989 m. 1H NMR (300 MHz, $CDCl_3$, 22 °C): $\delta = 7.86$ [s, 1H, C=C(H)], 4.74 (m, 1H, C_5H_4), 4.69 (m, 1H, C_5H_4), 4.45 (m, 2H, C_5H_4), 4.32 (m, 1H, C_5H_4), 4.31 (m, 2H, C_5H_4), 4.24 (s, 5H, C_5H_5), 4.20 (s, 5H, C_5H_5), 4.13 (m, 1H, C_5H_4), 0.36 (s, 9H, SiMe₃). MS (FAB⁺) m/z : 920 [M+H]⁺, 892–752 [M⁺-nCO, $n = 1-6$]. Anal. Calc. for $C_{35}H_{28}O_6SSiFe_2Ru_2$: C, 45.76; H, 3.08; S, 3.48. Found: C, 45.98; H, 3.53; S, 2.85. Spectral data for **4**: IR (toluene) cm^{-1} $\nu_{C=C}$: 2153 vw; ν_{CO} :

2075 m, 2046 vs, 2004 s, 1991 s, 1936 vw. 1H NMR (300 MHz, $CDCl_3$, 22 °C): $\delta = 7.55$ [s, 1H, C=C(H)], 4.57 (m, 2H, C_5H_4), 4.30 (m, 3H, C_5H_4), 4.28 (s, 5H, C_5H_5), 4.25 (m, 1H, C_5H_4), 4.22 (m, 1H, C_5H_4), 4.17 (m, 1H, C_5H_4), 4.13 (s, 5H, C_5H_5), 0.32 (s, 9H, SiMe₃). MS (FAB⁺) m/z : 920 [M+H]⁺, 836–752 [M⁺-nCO, $n = 3-6$]. Anal. Calc. for $C_{35}H_{28}O_6SSiFe_2Ru_2 \cdot 1/3C_6H_{14}$: C, 46.85; H, 3.44; S, 3.37. Found: C, 46.86; H, 3.72; S, 3.20%.

5.4. Synthesis of compound $Ru_2(CO)_6[\mu-\eta^2, \eta^4-(Me_3Si)C=C\{SC(Fc)=C(SC\equiv CSiMe_3)\}C=C(Fc)]$ (**5**)

A toluene solution (20 mL) of the compound $Ru_2(CO)_6[\mu_3-\eta^2, \eta^4, \eta^3-(Me_3Si)C=C\{SC(Fc)=C(SC\equiv CSiMe_3)Ru(CO)_3\}C=C(SiMe_3)]$ (45 mg, 0.04 mmol) was heated at 65 °C for 24 h. After removing the solvent *in vacuo*, the residue was chromatographed by TLC using hexane/toluene (5:1) as eluent yielding a red band corresponding to compound $Ru_2(CO)_6[\mu-\eta^2, \eta^4-(Me_3Si)C=C\{SC(Fc)=C(SC\equiv CSiMe_3)\}C=C(Fc)]$ **5** (18 mg, 0.02 mmol, 48%). Spectral data for **5**. IR (hexane) cm^{-1} $\nu_{C=C}$: 2099 vw; ν_{CO} : 2072 s, 2047 s, 2034 s, 2001 vs, 1990 s. 1H NMR (300 MHz, $CDCl_3$, 22 °C) $\delta = 5.54$ (m, 1H, C_5H_4), 4.91 (m, 1H, C_5H_4), 4.81 (m, 1H, C_5H_4), 4.52 (m, 1H, C_5H_4), 4.45 (m, 3H, C_5H_4), 4.40 (m, 1H, C_5H_4), 4.22 (s, 5H, C_5H_5), 4.17 (s, 5H, C_5H_5), 0.39 (s, 9H, SiMe₃), -0.02 (s, 9H, SiMe₃). MS (FAB⁺) m/z : 1048 [M+H]⁺, 992–879 [M⁺-nCO, $n = 2-6$]. Anal. Calc. for $C_{40}H_{36}O_6S_2Si_2Fe_2Ru_2 \cdot 1/4C_6H_{14}$: C, 46.65; H, 3.14; S, 5.99. Found: C, 46.61; H, 3.82; S, 5.49%.

5.5. Thermal reaction of $Ru_2(CO)_6[\mu_3-\eta^2, \eta^4, \eta^3-(Me_3Si)C=C\{SC(Fc)=C(SC\equiv CSiMe_3)Ru(CO)_3\}C=C(SiMe_3)]$ in the presence of $HC\equiv CFc$

A mixture of $Ru_2(CO)_6[\mu_3-\eta^2, \eta^4, \eta^3-(Me_3Si)C=C\{SC(Fc)=C(SC\equiv CSiMe_3)Ru(CO)_3\}C=C(SiMe_3)]$ (70 mg, 0.06 mmol) and $HC\equiv CFc$ (13 mg, 0.06 mmol) in toluene (15 mL) was heated at 65 °C for 4.5 h. After removing the solvent *in vacuo*, the residue was chromatographed by TLC using hexane/toluene (4:1) as eluent yielding a small amount of compound **5** followed by a red band corresponding to the compound $Ru_2(CO)_6[\mu-\eta^2, \eta^4-(Me_3Si)C=C\{SC(Fc)=C(SC\equiv CSiMe_3)C(H)=C(Fc)\}C=C(Fc)]$ **6** (10 mg, 0.01 mmol, 14%) and a third band of the known compound $1,2,4-C_6H_3(Fc)_3$ (20 mg, 0.02 mmol, 45%). Suitable crystals for X-ray diffraction of compound **6** were grown from hexane/toluene at -20 °C. Spectral data for **6**: IR (hexane) cm^{-1} $\nu_{C=C}$: 2092 vw, ν_{CO} 2072 m, 2043 vs, 2003 vs, 1995 s, 1939 vw. 1H NMR ($CDCl_3$, 300 MHz, 22 °C) δ 6.99 [s, 1H, C=C(H)], 4.91 (m, 1H, C_5H_4), 4.56 (m, 1H, C_5H_4), 4.44 (m, 1H, C_5H_4), 4.41 (m, 1H, C_5H_4), 4.36 (m, 1H, C_5H_4), 4.22 (s, 5H, C_5H_5), 4.14 (s, 5H, C_5H_5), 4.07 (m, 1H, C_5H_4), 3.98 (m, 6H, $C_5H_5 + C_5H_4$), 3.94 (m, 1H, C_5H_4), 3.85 (m, 1H, C_5H_4), 3.81 (m, 1H, C_5H_4), 3.79 (m, 1H, C_5H_4), 3.70 (m, 1H, C_5H_4), 0.49 (s, 9H, SiMe₃), 0.28 (s, 9H, SiMe₃). MS (MALDI) m/z : 1258 [M+H]⁺, 1230–1090 [M⁺-nCO, $n = 1-6$]. Anal. Calc. for $C_{52}H_{46}O_6S_2Si_2Fe_3Ru_2$: C, 49.72; H, 3.66; S, 5.09. Found: C, 49.65; H, 3.83; S, 4.82%.

5.6. X-ray structure determinations for complexes **1**, **3**, **4** and **6**

X-ray crystals of compounds **1**, **3**, **4** and **6** were grown as described in Section 5. Complexes were covered with a layer of a viscous perfluoropolyether (Fomblin® Y). A suitable crystal was selected with the aid of a microscope, mounted in a cryo loop, and immediately placed in the low-temperature nitrogen stream of the diffractometer at 200 K. The intensity data sets were collected on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit. Crystallographic data for all the complexes are presented in Table 2.

Table 2
Crystallographic data for complexes **1**, **3**, **4** and **6**.

| Compound | 1 | 3 | 4 | 6 |
|--|---|--|--|---|
| Empirical formula | C ₂₈ H ₂₈ Fe ₃ O ₆ SSi ₂ | C ₃₅ H ₂₈ Fe ₂ O ₆ Ru ₂ SSi | C ₃₅ H ₂₈ Fe ₂ O ₆ Ru ₂ SSi | C ₅₂ H ₄₆ Fe ₃ O ₆ Ru ₂ S ₂ Si ₂ |
| Formula weight | 716.29 | 918.56 | 918.56 | 1256.88 |
| Temperature (K) | 200 | 200 | 200 | 200 |
| λ (Mo K α) (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Triclinic | Monoclinic | Monoclinic | Triclinic |
| Space group | <i>P</i> $\bar{1}$ | <i>P</i> 2 ₁ / <i>n</i> | <i>P</i> 2 ₁ / <i>c</i> | <i>P</i> $\bar{1}$ |
| <i>a</i> (Å) | 9.509(2) | 21.295(5) | 10.5727(19) | 11.192(2) |
| <i>b</i> (Å) | 12.659(2) | 7.3090(7) | 25.273(5) | 12.140(2) |
| <i>c</i> (Å) | 14.844(2) | 23.180(4) | 13.7060(8) | 19.3975(16) |
| α (°) | 108.820(10) | | | 97.165(13) |
| β (°) | 90.700(10) | 104.356(11) | 110.631(8) | 97.853(14) |
| γ (°) | 109.900(10) | | | 103.88(3) |
| Volume (Å ³); <i>Z</i> | 1575.3(5); 2 | 3495.1(10); 4 | 3427.4(9); 4 | 2500.4(8); 2 |
| ρ_{calcd} [g cm ⁻³] | 1.51 | 1.746 | 1.780 | 1.669 |
| μ [mm ⁻¹] | 1.543 | 1.799 | 1.834 | 1.62 |
| <i>F</i> (000) | 732 | 1824 | 1824 | 1264 |
| Crystal size (mm) | 0.20 × 0.15 × 0.10 | 0.42 × 0.22 × 0.10 | 0.23 × 0.20 × 0.19 | 0.30 × 0.26 × 0.20 |
| θ Range | 3.32–27.5 | 3.0–27.5 | 3.0–27.5 | 3.0–27.5 |
| Index ranges | –12 to 12, –16 to 16, –19 to 19 | –27 to 26, –9 to 9, 0–30 | –13 to 12, –32 to 32, 0–17 | –14 to 14, –15 to 15, –25 to 25 |
| Collected reflections | 34202 | 45339 | 70845 | 38763 |
| Independent reflections | 7202 | 7974 | 7862 | 11467 |
| Reflections [<i>F</i> > 4 σ (<i>F</i>)] | 5389 | 2889 | 3193 | 6073 |
| Goodness-of-fit on <i>F</i> ² | 1.042 | 0.925 | 0.909 | 0.968 |
| Final <i>R</i> indices | <i>R</i> ₁ = 0.034 <i>wR</i> ₂ = 0.078 | <i>R</i> ₁ = 0.090 <i>wR</i> ₂ = 0.184 | <i>R</i> ₁ = 0.076 <i>wR</i> ₂ = 0.121 | <i>R</i> ₁ = 0.068 <i>wR</i> ₂ = 0.149 |
| <i>R</i> indices (all data) | <i>R</i> ₁ = 0.057 <i>wR</i> ₂ = 0.085 | <i>R</i> ₁ = 0.228 <i>wR</i> ₂ = 0.245 | <i>R</i> ₁ = 0.206 <i>wR</i> ₂ = 0.154 | <i>R</i> ₁ = 0.155 <i>wR</i> ₂ = 0.188 |
| Largest difference in peak/hole (e Å ⁻³) | 0.378/–0.624 | 1.48/–1.69 | 1.03/–1.12 | 1.40/–1.15 |

Complexes **3** and **4** diffracted very weakly, preventing a very precise determination. The structures were solved, using the WINGX [26] package, direct methods (SHELXS-97) [27] and refined by least-squares against *F*² (SHELXL-97) [27]. Absorption correction procedures were carried out using the multiscan SORTAV [28] program. All the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included, positioned geometrically, and refined by using a riding model.

6. Supplementary material

CCDC 694320, 694321, 694322 and 694323 contain the supplementary crystallographic data for compounds **1**, **3**, **4** and **6** respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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