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Oxidative addition reactions of 2,2′-bithiophene and 2,2′ : 5′,2″-terthiophene with trinuclear clusters of iron, ruthenium and osmium

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Abstract

Reactions of the cluster $[Os_3(CO)_{10}(MeCN)_2]$ with 2,2′-bithiophene ($C_8H_6S_2$) and 2,2′ : 5′,2″-terthiophene ($C_{12}H_8S_3$) lead to the decacarbonyl complexes $[Os_3(\mu\text{-}H)(C_8H_5S_2)(CO)_{10}]$ and $[Os_3(\mu\text{-}H)(C_{12}H_7S_3)(CO)_{10}]$, respectively, which are formed by C–H bond cleavage. Upon heating these compounds, decarbonylation occurs to afford high yields of the corresponding nonacarbonyl species $[Os_3(\mu\text{-}H)_2(C_8H_4S_2)(CO)_9]$ and $[Os_3(\mu\text{-}H)_2(C_{12}H_6S_3)(CO)_9]$. In contrast, the reaction of 2,2′-bithiophene with $[Ru_3(CO)_{12}]$ leads to the dimer $[Ru_2(C_8H_6S)(CO)_6]$ by cleavage of the C–S bond and extrusion of the heteroatom. The cluster $[Fe_3(CO)_{12}]$ reacts with 2,2′-bithiophene and 2,2′ : 5′,2″-terthiophene to give $[Fe_2(C_8H_6S_2)](CO)_6]$, $[Fe_2(C_8H_6S)(CO)_6]$, $[Fe_2(C_{12}H_8S_3)(CO)_6]$ and $[Fe_2(C_{12}H_8S_2)(CO)_6]$ respectively, for which insertion of the metal atom in a C–S bond or extrusion of the heteroatom occurs.

Key words: Osmium; Iron; Ruthenium; Oxidative addition; Thiophene; Carbonyl

1. Introduction

Thiophene is known to bind to single metal atoms in an η^1, η^4 or η^5 manner [1], but few studies have been made with transition metal clusters [2]. The cluster $[Fe_3(CO)_{12}]$ reacts with thiophene with loss of the sulfur atom to give a ferrole compound $[Fe_2(\mu\text{-}C_4H_4)(CO)_6]$, while $[Fe_2(\mu\text{-}C_4H_3MeS)(CO)_6]$ as well as the sulfur-free species $[Fe_2(\mu\text{-}C_4H_3Me)(CO)_6]$ are formed from 2-methylthiophene. Insertion of an iron atom into the less hindered C–S bond occurred to give the ring-opened thiophene derivative. We recently reported the reaction of $[Ru_3(CO)_{12}]$ with 2-methylthiophene [3] to give the sulfur-free species $[Ru_2(\mu\text{-}C_4H_3Me)(CO)_6]$, clearly derived by C–S bond cleavage as in the iron case, as well as the tetranuclear cluster $[Ru_4(\mu_3\text{-}S)(\mu\text{-}C_4H_3Me)(CO)_{11}]$ which contains separated S and C_4H_3Me ligands. In contrast, we have shown that thiophene does not undergo ring-opening with $[Os_3(CO)_{12}]$ or $[Os_3(CO)_{10}(MeCN)_2]$ but undergoes exclusively C–H bond cleavage to yield the thienyl isomers $[Os_3(\mu\text{-}H)(\mu\text{-}C_4H_3S)(CO)_{10}]$ (*exo* and *endo* isomers in rapid equilibrium) which lose CO to give the cluster $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}C_4H_2S)(CO)_9]$, which contains a triple-bridged cyclic alkyne ligand [4,5] related to μ_3-benzyne.

We have now examined related reactions with 2,2′-bithiophene and 2,2′ : 5′,2″-terthiophene because of the importance of the hydrodesulfurization (HDS) process, which requires C–S bond cleavage. The elucidation of the mechanism of such desulfurization provides the impetus for much of the current work on thiophene complexes.

The bis-acetonitrile complex $[Os_3(CO)_{10}(MeCN)_2]$ reacts with 2,2′-bithiophene and 2,2′ : 5′,2″-terthiophene in cyclohexane to give the oxidative addition products

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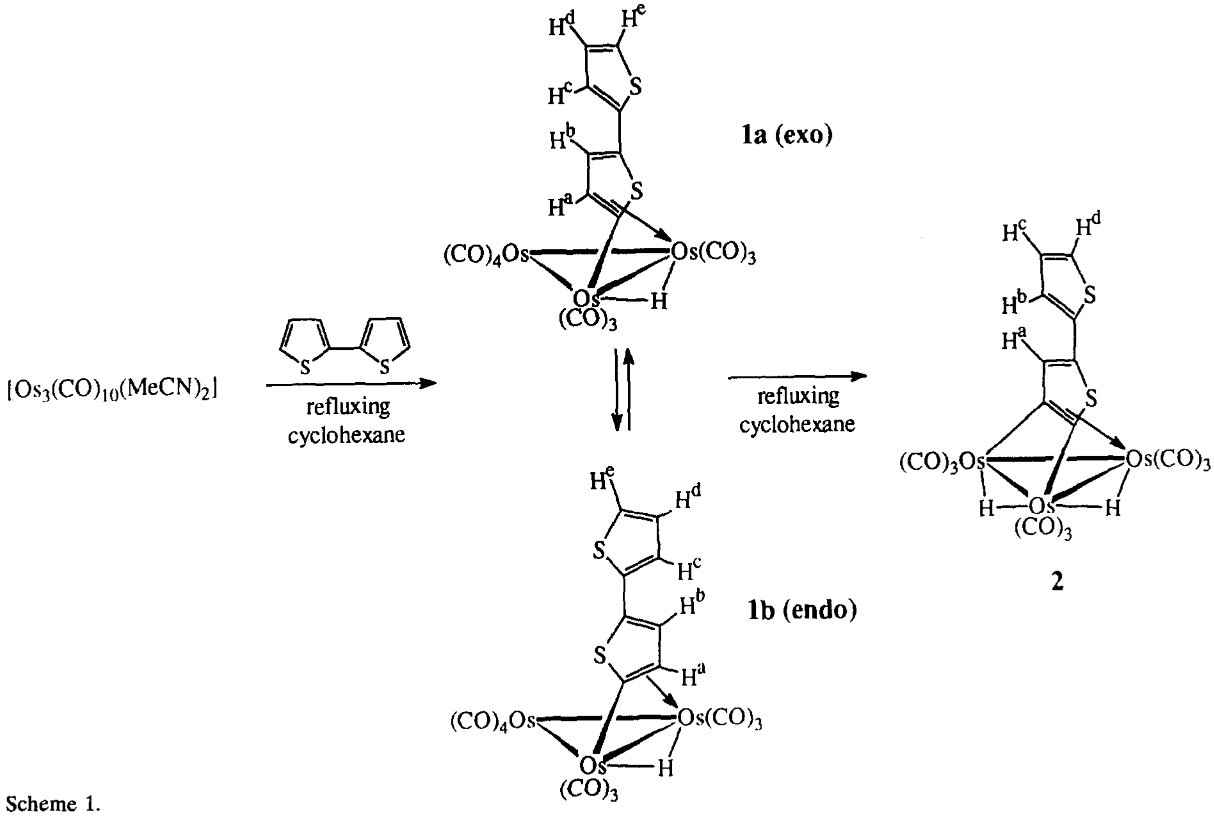


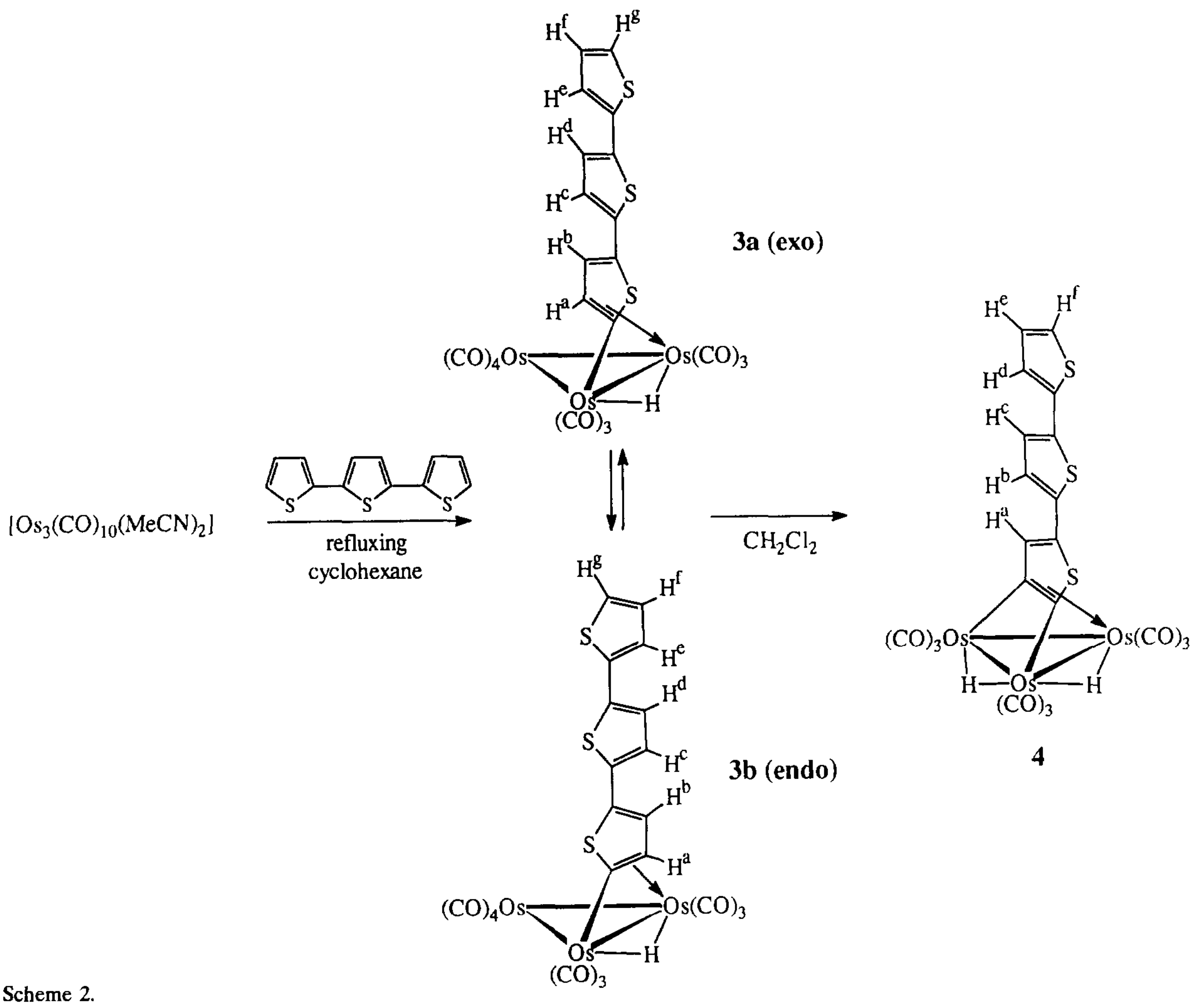
Scheme 1.

$[Os_3(\mu\text{-}H)(\mu\text{-}C_4H_2S\text{-}C_4H_3S)(CO)_{10}]$ **1a**, **1b** and $[Os_3(\mu\text{-}H)(\mu\text{-}C_4H_2S\text{-}C_4H_2S\text{-}C_4H_3S)(CO)_{10}]$ **3a**, **3b**, respectively, exclusive C–H bond cleavage having occurred to afford thienyl isomers (*exo* and *endo* isomers in rapid equilibrium). In addition, low yields were obtained of the decarbonylation products $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}C_4HS\text{-}C_4H_3S)(CO)_9]$ **2**, and $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}C_4HS\text{-}C_4H_2S\text{-}C_4H_3S)(CO)_9]$, **4**, respectively, as shown in Schemes 1 and 2.

On the basis of the ^1H NMR and IR data (Table 1) and the X-ray structure of the analogous species derived from 2-methylthiophene [6], we identified compounds **1a** and **3a** as having a similar structure, with the S-atom *exo*. Although a single set of coalesced NMR signals was observed at room temperature and above, the spectrum showed separated resonances for two isomers at −40°C, indicating that these are the *endo* and *exo* forms that are in rapid equilibrium at room temperature. The relative concentrations of the thienyl compounds are 67% **1a**, 33% **1b**, 65% **3a**, and 35% **3b** (see Table 1). We have previously discussed the mechanism of this type of *exo–endo* interconversion of μ-thienyl ligands, and have proposed S-bonded intermediates on the grounds that the rate for the corresponding furyl compounds is much lower. No products resulting from S–C bond cleavage were detected.

Heating of clusters **1** and **3** results in quantitative formation of the nonacarbonyl clusters **2** and **4**, as indicated by the ^1H NMR and IR data and the X-ray structure of the dehydrogenated form of thiophene in the cluster $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}C_4H_2S)(CO)_9]$ which we reported earlier [4].

The compound $[Ru_3(CO)_{12}]$ reacts with 2,2'-bithiophene in refluxing cyclohexane to give exclusively a dimer, $[Ru_2(\mu\text{-}C_4H_3\text{-}C_4H_3S)(CO)_6]$, **5**, in which the bithiophene ligand has lost a sulfur atom. On the basis of the ^1H NMR and IR data the structure depicted in Scheme 3 is the most favoured. The reaction of 2,2'-bithiophene and $[Fe_3(CO)_{12}]$ was re-examined [7]. It was found to proceed as described previously to give, as orange crystals, the thiaferrole derivative $[Fe_2(\mu\text{-}C_4H_3S\text{-}C_4H_3S)(CO)_6]$, **6**, which has been characterized by single-crystal X-ray diffraction. However, under our working conditions (see Experimental details), the ferrole derivative $[Fe_2(\mu\text{-}C_4H_3\text{-}C_4H_3S)(CO)_6]$ **7** was also obtained as a yellow solid (Scheme 4). The ^1H NMR data for the thiaferrole derived from 2,2'-bithiophene match those reported previously [7]. The ^1H NMR spectrum of the ferrole derivative (Fig. 1) is very



Scheme 2.

similar to that of the corresponding compound obtained by the reaction of 2,2'-bithiophene and $[Ru_3(CO)_{12}]$. The insertion of a ruthenium or an iron atom into the S–C bond is regiospecific, the metal atom inserting into the less hindered S–C bond.

We were unable to obtain any isolable products from the reaction of $[Ru_3(CO)_{12}]$ and 2,2' : 5',2''-terthiophene. However, from the reaction of $[Fe_3(CO)_{12}]$ with 2,2' : 5',2''-terthiophene two products were isolated, that are related to those obtained with 2,2'-bithiophene. On the basis of the ^1H NMR and IR data (Table 1) the structures shown for $[Fe_2(\mu\text{-}C_4H_3S\text{–}C_4H_2S\text{–}C_4H_3S)(CO)_6]$, **8**, and $[Fe_2(\mu\text{-}C_4H_3\text{–}C_4H_2S\text{–}C_4H_3S)(CO)_6]$, **9**, are the most favoured.

Our observations on the chemistry of 2,2'-bithiophene and of 2,2' : 5',2''-terthiophene with the trinuclear carbonyls of iron, ruthenium and osmium failed to provide evidence of reaction at more than one thiophene ring to give ligand bridges between di- or tri-nuclear metal systems. In essence, the chemistry is closely related to that of thiophene itself.

2. Experimental details

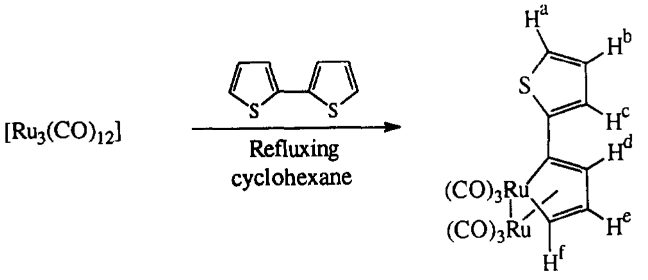
2.1. Osmium with 2,2'-bithiophene

A solution of $[Os_3(CO)_{10}(MeCN)_2]$ (0.100 g, 0.107 mmol) and 2,2'-bithiophene (0.035 g, 0.211 mmol) in cyclohexane (30 cm^3) was refluxed under nitrogen for 20 min, after which the colour of the solution had changed from yellow to deep green. Removal of the solvent under reduced pressure and TLC separation [SiO_2; eluent, petroleum ether (b.p. 40–60°C)] gave three main bands. The fastest band gave the cluster $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}C_4HS\text{–}C_4H_3S)(CO)_9]$ **2** (0.028 g, 0.028 mmol, 26%) as a yellow solid. The second band contained the excess of ligand, and the third was identified

TABLE 1. IR and ^{1}H NMR data for the new complexes

Compound	ν(CO) ^{a}/(cm^{-1})	^{1}H NMR ^{b}	J(Hz)
$[Os_3(\mu\text{-}H)(\mu\text{-}C_4H_2S\text{–}C_4H_3S)(CO)_{10}]$ **(1a)** + **(1b)**	2101w, 2064ms, 2052s, 2018ms, 2007m, 1991m, 1982sh.	*exo* (67%) ^{c} 8.02(d, H ^{a}) 7.73(d, H ^{e}) 7.60(d, H ^{c}) 7.19(d, H ^{b}) 7.16(m, H ^{d}) −14.9(s, OsH) *endo* (33%) ^{c} 8.95(d, H ^{a}) 7.96(d, H ^{e}) 7.89(d, H ^{c}) 7.73(d, H ^{b}) 7.20(m, H ^{d}) −14.4(s, OsH)	J_{ab} 3.3 J_{cd} 3.7 J_{ce} 0.8 J_{de} 5.1 J_{ab} 3.9 J_{cd} 4.0 J_{ce} 0.6 J_{de} 4.7
$[Os_3(\mu\text{-}H)_2(\mu_3\text{-}C_4HS\text{–}C_4H_3S)(CO)_9]$ **(2)**	2111m, 2083s, 2059ms, 2036s, 2028sh, 2011s, 2001m, 1988m	7.56(s, H ^{a}) 7.50(dd, H ^{b}) 7.31(dd, H ^{d}) 7.08(dd, H ^{c}) −18.9(s, OsH)	J_{bc} 5.1 J_{bd} 1.3 J_{cd} 3.6
$[Os_3(\mu\text{-}H)(\mu\text{-}C_4H_2S\text{–}C_4H_2S\text{–}C_4H_3S)(CO)_{10}]$ **(3a)** + **(3b)**	2101m, 2074w, 2063ms, 2051s, 2026sh, 2027ms, 2008sh, 1991s, 1983sh.	*exo* (65%) ^{d} 8.36(br, H ^{a}) 7.39(br, H ^{b}) 7.20(dd, H ^{g}) 7.15(dd, H ^{e}) 7.05(m, H ^{c}H ^{d}) 7.02(m, H ^{f}) −14.6(br, OsH) *endo* (35%) ^{d,e} 8.36(br, H ^{a}) 7.39(br, H ^{b}) 7.27(dd, H ^{g}) 7.25(m, H ^{e}) 7.11(s, H ^{d}) 7.09(s, H ^{c}) 7.00(dd, H ^{f}) −14.6(br, OsH)	J_{ef} 3.7 J_{eg} 1.2 J_{fg} 5.1
$[Os_3(\mu\text{-}H)_2(\mu\text{-}C_4HS\text{–}C_4H_2S\text{–}C_4H_3S)(CO)_9]$ **(4)**	2111w, 2082s, 2058ms, 2036m, 2028w, 2010m, 2001w, 1987w.	7.26(s, H ^{a}) 7.22(dd, H ^{f}) 7.16(dd, H ^{d}) 7.06(s, H ^{b} H ^{c}) 7.00(dd, H ^{e}) −19.1(s, OsH)	J_{df} 1.2 J_{de} 3.6 J_{ef} 5.1
$[Ru_2(\mu\text{-}C_4H_3\text{–}C_4H_3S)(CO)_6]$ **(5)**	2084m, 2055s, 2021sh, 2015s, 1991w, 1987w.	7.15(dd, H ^{a}) 7.04(dd, H ^{c}) 7.01(dd, H ^{e}) 6.87(dd, H ^{b}) 6.48(t, H ^{d}) 6.42(dd, H ^{f})	J_{ab} 5.1 J_{ac} 1.2 J_{bc} 3.6 J_{df} 2.4 J_{ed} 2.3 J_{ef} 6.3
$[Fe_2(\mu\text{-}C_4H_3S\text{–}C_4H_3S)(CO)_6]$ **(6)**	2078m, 2045ms, 2009sh, 2000ms, 1993w.	9.23(d, H ^{f}) 7.40(dd, H ^{a}) 7.20(dd, H ^{c}) 7.01(dd, H ^{b}) 6.66(d, H ^{d}) 5.37(dd, H ^{e})	J_{ab} 4.9 J_{ac} 1.0 J_{bc} 3.8 J_{de} 5.5 J_{ef} 8.8
$[Fe_2(\mu\text{-}C_4H_3\text{–}C_4H_3S)(CO)_6]$ **(7)**	2074w, 2039ms, 2005s, 1997m, 1955w.	7.38(dd, H ^{a}) 7.12(dd, H ^{c}) 7.02(dd, H ^{e}) 6.96(dd, H ^{b}) 6.60(dd, H ^{f}) 6.54(dd, H ^{d})	J_{ab} 4.9 J_{ac} 1.1 J_{bc} 3.5 J_{ef} 5.4 J_{de} 2.2 J_{df} 2.3
$[Fe_2(\mu\text{-}C_4H_3S\text{–}C_4H_2S\text{–}C_4H_3S)(CO)_6]$ **(8)**	2078m, 2045ms, 2009sh, 2006m, 1993w.	9.25(d, H ^{h}) 7.43(dd, H ^{c}) 7.26(dd, H ^{a}) 7.16(s, H ^{e} H ^{d}) 7.05(dd, H ^{b}) 6.69(d, H ^{f}) 5.40(dd, H ^{g})	J_{ab} 3.7 J_{ac} 1.0 J_{bc} 5.0 J_{fg} 5.5 J_{gh} 8.7
$[Fe_2(\mu\text{-}C_4H_3\text{–}C_4H_2S\text{–}C_4H_3S)(CO)_6]$ **(9)**	2073w, 2039ms, 2005s, 1997m.	7.43(dd, H ^{a}) 7.28(dd, H ^{c}) 7.08(m, H ^{b} H ^{d} H ^{e} H ^{f}) 6.62(dd, H ^{g}) 6.59(t, H ^{h})	J_{ab} 4.9 J_{ac} 1.1 J_{bc} 3.3 J_{de} 3.7 J_{fg} 5.5 J_{fh} 2.2 J_{gh} 2.7

[a] Recorded in cyclohexane. [b] In $CDCl_3$ at room temperature unless stated otherwise. [c] In CD_3COCD_3 at −40°C. [d] Data for $CDCl_3$ solution. In CD_3COCD_3 at −40°C: major isomer: δ 8.03(dd, H ^{a}) 7.90(dd, H ^{b}), −14.9(s, OsH); minor isomer: δ 9.00(dd, H ^{a}) 7.74(dd, H ^{b}), −14.8(s, OsH). [e] Couplings not resolved.



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Scheme 3.

as the mixture of isomers of $[Os_3(\mu\text{-}H)(\mu\text{-}C_4H_2S\text{-}C_4H_3S)(CO)_{10}]$, **1a** and **1b** (0.066 g, 0.065 mmol, 61%), as a green solid.

2.2. *Thermolysis of compound 1.*

A solution of compound **1** (0.025 g, 0.025 mmol) in *n*-octane (30 cm^3) was heated under reflux under nitrogen for 30 min. Removal of the solvent under reduced pressure and TLC separation as above gave two pale-yellow bands yielding the cluster $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}C_4HS\text{-}C_4H_3S)(CO)_9]$, **2** (0.019 g, 0.019 mmol, 76%) as a yellow solid, and some unchanged **1**.

2.3. *Osmium with 2,2′:5′,2″-terthiophene*

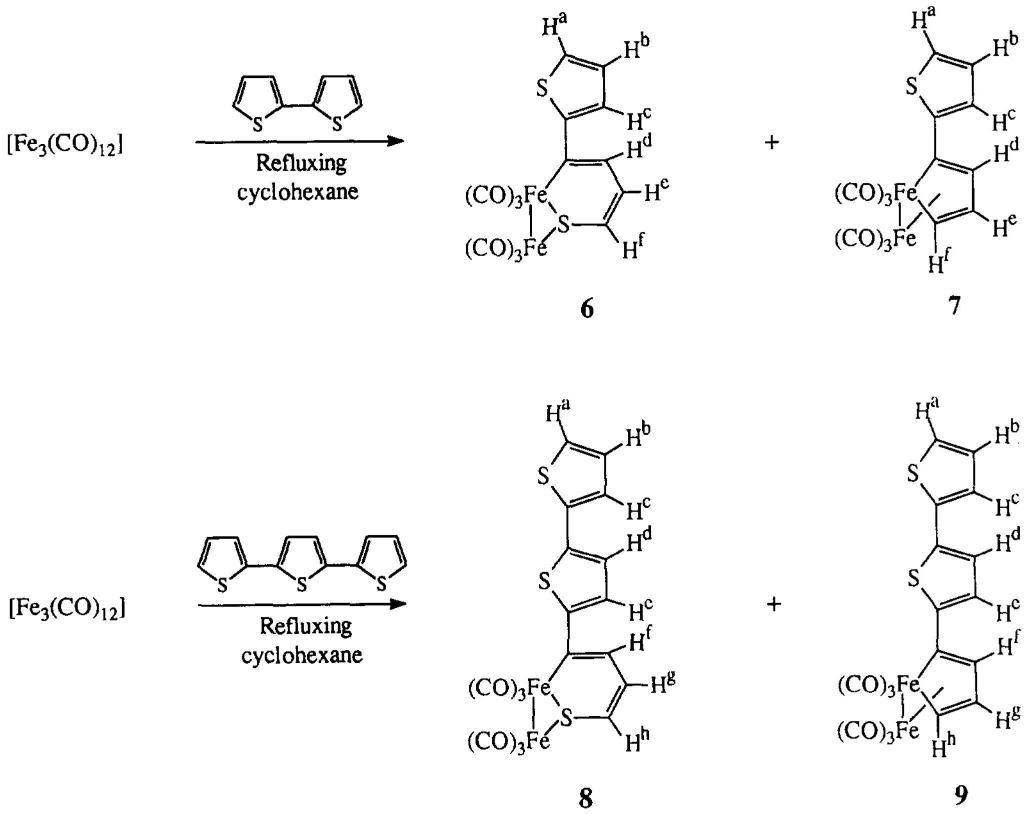
A solution of $[Os_3(CO)_{10}(MeCN)_2]$ (0.150 g, 0.16 mmol) and 2,2′:5′,2″-terthiophene (0.065 g, 0.26 mmol) in cyclohexane (30 cm^3) was refluxed under nitrogen for 3 h, during which the colour changed from yellow to purple. After removal of the solvent, the residue was separated by TLC as above to give a mixture of isomers of $[Os_3(\mu\text{-}H)(\mu\text{-}C_4H_2S\text{-}C_4H_2S\text{-}C_4H_3S)(CO)_{10}]$, **3a** and **3b** (0.048 g, 0.044 mmol, 27%) as a purple solid.

2.4. *Decarbonylation of compound 3*

A dichloromethane solution of the isomers **3a** and **3b** was left for 15 days at room temperature. TLC work-up gave $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}C_4HS\text{-}C_4H_2S\text{-}C_4H_3S)(CO)_9]$, **4**, (17%) as a yellow solid and some unchanged purple material.

2.5. *Ruthenium with 2,2′-bithiophene*

A solution of $[Ru_3(CO)_{12}]$ (0.150 g, 0.235 mmol) and 2,2′-bithiophene (0.090 g, 0.36 mmol) in cyclohexane (50 cm^3) was refluxed under nitrogen for 24 h. Removal of the solvent under reduced pressure and TLC separation of the brown residue [SiO_2; eluent,



Scheme 4.

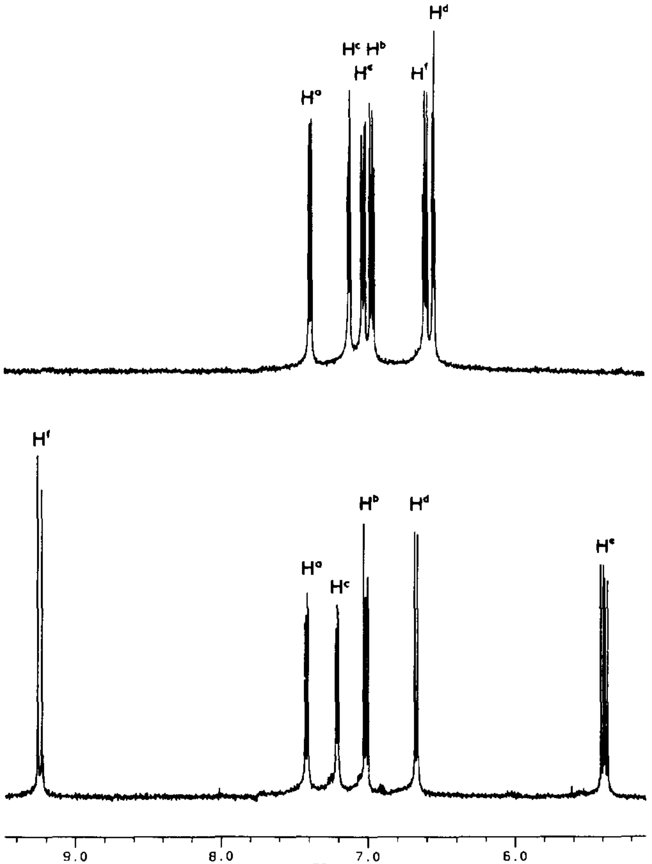


Fig. 1. Extrusion of the S-atom leads to a major change in the ^1H NMR spectra. Bottom spectrum: $[Fe_2(\mu\text{-}C_4H_3S\text{-}C_4H_3S)(CO)_6]$, **6**; top spectrum: $[Fe_2(\mu\text{-}C_4H_3\text{-}C_4H_3S)(CO)_6]$, **7**.

petroleum ether (b.p. 40–60°C)] gave one main yellow band yielding $[Ru_2(\mu\text{-}C_4H_3\text{-}C_4H_3S)(CO)_6]$, **5**, as a yellow solid (0.037 g, 0.069 mmol, 20%).

2.6. Iron with 2,2'-bithiophene

2,2'-bithiophene (0.090 g, 0.36 mmol) was added to a refluxing solution of $[Fe_3(CO)_{12}]$ (0.200 g, 0.397 mmol) in cyclohexane (30 cm^3) under nitrogen. After 24 h filtration of a solid metallic residue, removal of the solvent from the filtrate, and TLC separation [SiO_2; eluent, petroleum ether (b.p. 40–60°C)] gave two main bands, which yielded $[Fe_2(\mu\text{-}C_4H_3S\text{-}C_4H_3S)(CO)_6]$ **6** (0.046 g, 0.103 mmol, 19%) as an orange solid and $[Fe_2(\mu\text{-}C_4H_3\text{-}C_4H_3S)(CO)_6]$ **7** (0.092 g, 0.22 mmol, 41%) as a yellow solid.

2.7. Iron with 2,2' : 5',2"-terthiophene

A solution of $[Fe_3(CO)_{12}]$ (0.060 g, 0.12 mmol) and 2,2' : 5',2"-terthiophene (0.070 g, 0.28 mmol) in cyclohexane (30 cm^3) was refluxed under nitrogen for 24 h, during which the colour changed from green to orange. After filtration of a solid metallic residue and removal of the solvent, TLC separation [SiO_2; eluent, petroleum ether (b.p. 40–60°C)] gave $[Fe_2(\mu\text{-}C_4H_3S\text{-}C_4H_2S\text{-}C_4H_3S)(CO)_6]$ **8** as a yellow solid (0.006 g, 0.011 mmol, 6%) and $[Fe_2(\mu\text{-}C_4H_3\text{-}C_4H_2S\text{-}C_4H_3S)(CO)_6]$ **9** as an orange solid (0.036 g, 0.073 mmol, 40%).

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