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Synthesis and molecular structures of $S_2Fe_2(CO)_6$ heterometallic derivatives, containing $(Ph_3P)_2Pt$ or CpRe(CO) fragments

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Abstract

The heterometallic cluster $(Ph_3P)_2Pt(\mu_3-S)_2Fe_2(CO)_6$ (II) has been synthesized by transmetallation of $S_2Fe_3(CO)_9$ under the action of $(Ph_3P)_2PtCl_2$. X-ray studies indicate that II contains a short Fe-Fe bond (mean 2.496(7) Å for 4 independent molecules), but that there are no bonds between Fe and Pt. It is concluded that transmetallation takes place via a process of coordination of $(Ph_3P)_2PtCl_2$ with a lone pair of the μ_3 -S bridge in $S_2Fe_3(CO)_9$; this is because of the absence of any analogous reaction of $(Ph_3P)_2PtCl_2$.

The trinuclear cluster $CpRe(\mu-CO)(\mu_3-S)_2Fe_2(CO)_6$ (III) has been obtained by the interaction of $CpRe(CO)_2(THF)$ with $S_2Fe_2(CO)_6$. According to X-ray studies this cluster contains short Re-Fe bonds (mean 2.712(2) Å), but does not contain an Fe-Fe bond. It was concluded that the distinctive features of the metal-core character of $LM(\mu_3-S)_2Fe_2(CO)_6$ clusters depend on the electron deficit of the LM fragments.

1. Introduction

The binuclear complex $S_2Fe_2(CO)_6$ (I), containing S–S and Fe–Fe bonds (2.007 and 2.552 Å, respectively) [1] has been used by us [2] and by other authors [3] for the planned synthesis of $LM(\mu_3-S)_2Fe_2(CO)_6$ clusters. Here we report the synthesis and some of the features of the molecular structures of this type of cluster, where $LM = (Ph_3P)_2Pt$ or CpRe(CO).

2. Results and discussion

The process of transmetallation of $S_2Fe_3(CO)_9$ under the action of $(Ph_3P)_2PtCl_2$ involves exchange of acidic ligands between Pt^{II} and terminal Fe^{II} ions with the formation of the cluster of $(Ph_3P)_2Pt(\mu_3-S)_2Fe_2(CO)_6$ (II). II had been previously obtained by reaction of $S_2Fe_2(CO)_6^{2-7}$ with $(Ph_3P)_2PtCl_2$ [4] and



Fig. 1. The structure of the cluster $(Ph_3P)_2Pt(\mu_3-S)_2Fe_2(CO)_6$ (II) (one from 4 independent molecules).

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TABLE 1. Bond lengths (Å) for the cluster $(Ph_3P)_2Pt(\mu_{3^{-1}}S)_2Fe_2(CO)_6$ (II)

Pt(1)-S(1)	2.315(9)	Fe(1) - S(2)	2.30(1)	
Pt(1)-S(2)	2.32(1)	Fe(2) - S(1)	2.29(1)	
Pt(1)-P(1)	2.302(9)	Fe(2) - S(2)	2.28(1)	
Pt(1) - P(2)	2.275(9)	Fe(3)-Fe(4)	2,499(8)	
Pt(2)-S(3)	2.37(1)	Fe(3)-S(3)	2.28(1)	
Pt(2)-S(4)	2.322(9)	Fe(3)-S(4)	2.24(1)	
Pt(2)-P(3)	2.323(9)	Fe(4)-S(3)	2.29(1)	
Pt(2)-P(4)	2.307(9)	Fe(4) - S(4)	2.28(1)	
Pt(3)-S(5)	2.32(1)	Fe(5)-Fe(6)	2.506(8)	
Pt(3) - S(6)	2.310(9)	Fe(5) - S(5)	2.30(1)	
Pt(3) - P(5)	2.32(1)	Fe(5)-S(6)	2.27(1)	
Pt(3) - P(6)	2.27(1)	Fe(6)-S(5)	2.32(1)	
Pt(4)-S(7)	2.374(9)	Fe(6)S(6)	2.28(1)	
Pt(4)–S(8)	2.326(9)	Fe(7)-Fe(8)	2.494(7)	
Pt(4)-P(7)	2.25(1)	Fe(7)-S(7)	2.30(1)	
Pt(4)-P(8)	2.282(9)	Fe(7)-S(8)	2.31(1)	
Fe(1)-Fe(2)	2.484(7)	Fe(8)-S(7)	2.31(1)	
Fe(1) - S(1)	2.29(1)	Fe(8) = S(8)	2.27(1)	
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Fig. 2. The structure of the cluster $CpRe(\mu - CO)(\mu_3 - S)_2Fe_2(CO)_6$ (III) (one from 2 independent molecules).

TABLE 2. Bond angles (°) for the cluster $(Ph_3P)_2Pt(\mu_3-S)_2Fe_2(CO)_6$ (II)

S(1) - Pt(1) - S(2)	75.5(3)	Fe(6) - Fe(5) - S(5)	57.6(3)	TABLE
S(1) - Pt(1) - P(1)	166.8(3)	Fe(6) - Fe(5) - S(6)	56.8(3)	S), Fe-(
S(2) - Pt(1) - P(1)	91.3(3)	S(5) - Fe(5) - S(6)	76.2(4)	5/21 020
S(1)-Pt(1)-P(2)	95.7(3)	Fe(5) - Fe(6) - S(5)	56.7(3)	Re(1)-2
S(2) - Pt(1) - P(2)	171.2(3)	Fe(5) - Fe(6) - S(6)	56.4(3)	Re(1)
P(1)-Pt(1)-P(2)	97.5(3)	S(5) - Fe(6) - S(6)	75.6(4)	Re(1)
S(3) - Pt(2) - S(4)	75.5(3)	Fe(8) - Fe(7) - S(7)	57.4(3)	Re(1)-
S(3) - Pt(2) - P(3)	91.(93)	Fe(8) - Fe(7) - S(8)	56.2(3)	Re(1)-
S(4) - Pt(2) - P(3)	147.3(3)	S(7)-Fe(7)-S8	78.6(4)	Re(2)-
S(3) - Pt(2) - P(4)	169.5(3)	Fe(7) - Fe(8) - S(7)	57.0(3)	Re(2)-1
S(4) - Pt(2) - P(4)	93.9(3)	Fe(7)-Fe(8)-S(8)	57.7(3)	Re(2)
P(3)-Pt(2)-P(4)	98.6(3)	S(7) - Fe(8) - S(8)	79.1(4)	Re(2)-
S(5) - Pt(3) - S(6)	75.1(3)	Pt(1)=S(1)=Fe(1)	92.2(3)	Re(2)-
S(5) - Pt(3) - P(5)	90.7(4)	Pt(1)-S(1)-Fe(2)	95.8(4)	Fe(1)-5
S(6) - Pt(3) - P(5)	165.8(4)	Fe(1)-S(1)-Fe(2)	65.8(3)	Fe(1)-6
S(5) - Pt(3) - P(6)	169.0(3)	Pt(1) - S(2) - Fe(1)	91.8(4)	Fe(1)=0
S(6) - Pt(3) - P(6)	94.8(3)	Pt(1)=S(2)=Fe(2)	95.6(4)	Fe(2)-5
P(5) - Pt(3) - P(6)	99.3(4)	Fe(1)-S(2)-Fe(2)	65.7(3)	Fe(2)-6
S(7) - Pt(4) - S(8)	76.7(3)	Pt(2) - S(3) - Fe(3)	91.1(4)	Fe(2)-0
S(7) - Pt(4) - P(7)	170.8(3)	Pt(2) = S(3) = Fe(4)	92.2(4)	Fe(3)-5
S(8) - Pt(4) - P(7)	94.2(3)	Fe(3) - S(3) - Fe(4)	66.2(3)	Fe(3)-6
S(7) - Pt(4) - P(8)	92.1(3)	Pt(2)=S(4)=Fe(3)	93.4(4)	Fe(4)-3
S(8) - Pt(4) - P(8)	168.6(4)	Pt(2) = S(4) = Fe(4)	93.8(3)	Fe(4)-6
P(7) - Pt(4) - P(8)	97.1(4)	Fe(3) - S(4) - Fe(4)	67.1(3)	Fe(4)-6
Fe(2)-Fe(1)-S(1)	57.0(3)	Pt(3)=S(5)=Fe(5)	93.7(4)	O(11)-
Fe(2) - Fe(1) - S(2)	56.9(3)	Pt(3) = S(5) = Fe(6)	93.9(4)	O(13)-
S(1) - Fe(1) - S(2)	76.4(4)	Fe(5)-S(5)-Fe(6)	65.7(3)	O(22)-
Fe(1)-Fe(2)-S(1)	57.2(3)	Pt(3) - S(6) - Fe(5)	94.6(4)	O(24)-
Fe(1)-Fe(2)-S(2)	57.5(3)	Pt(3)-S(6)-Fe(6)	95.2(4)	O(32)-
S(1) - Fe(2) - S(2)	76.8(4)	Fe(5) - S(6) - Fe(6)	66.8(3)	O(41)-
Fe(4) - Fe(3) - S(3)	57.1(3)	Pt(4) = S(7) = Fe(7)	92.3(4)	O(43)
Fe(4) - Fe(3) - S(4)	57.2(3)	Pt(4) - S(7) - Fe(8)	90.3(3)	C(1)-C
S(3) = Fe(3) = S(4)	78.8(4)	Fe(7)-S(7)-Fe(8)	65.6(3)	C(2)-C
Fe(3)-Fe(4)-S(3)	56.7(3)	Pt(4) - S(8) - Fe(7)	93.3(4)	C(4)-C
Fe(3)-Fe(4)-S(4)	55.8(3)	Pt(4) - S(8) - Fe(8)	92.5(4)	C(6)-C
S(3) - Fe(4) - S(4)	77.8(4)	Fe(7) - S(8) - Fe(8)	66.1(3)	C(8)-C

TABLE 3. Bond lengths (Å) for the cluster $CpRe(\mu-CO)(\mu_3-S)_2Fe_2(CO)_6$ (III)

$\overline{\text{Re}(1)}$ -Fe(1)	2.736(2)	Re(1)-Fe(2)	2.695(2)
Re(1)-S(1)	2.340(3)	Re(1) - S(2)	2.353(3)
Re(1)-C(1)	2.292(16)	Re(1) - C(2)	2.326(14)
Re(1)-C(3)	2.286(13)	Re(1) - C(4)	2.218(13)
Re(1) - C(5)	2.277(13)	Re(1)-C(24)	1.830(14)
Re(2)-Fe(3)	2.727(2)	Re(2)-Fe(4)	2.695(2)
Re(2) - S(3)	2.343(3)	Re(2) - S(4)	2.340(3)
Re(2)C(6)	2.305(11)	Re(2)–C(7)	2.289(15)
Re(2)-C(8)	2.224(11)	Re(2) - C(9)	2.306(12)
Re(2)-C(10)	2.265(12)	Re(2) = C(44)	1.909(14)
Fe(1) = S(1)	2.275(4)	Fe(1)-S(2)	2.276(3)
Fe(1) - C(11)	1.810(13)	Fe(1) - C(12)	1.797(14)
Fe(1) = C(13)	1.805(11)	Fe(2) = S(1)	2.277(3)
Fe(2)-S(2)	2.289(4)	Fe(2)-C(21)	1.805(14)
Fe(2)C(22)	1.795(13)	Fe(2)–C(23)	1.820(12)
Fe(2)–C(24)	2.383(16)	Fe(3)=S(3)	2.265(3)
Fe(3)-S(4)	2.274(4)	Fe(3)-C(31)	1.817(13)
Fe(3)-C(32)	1.795(15)	Fe(3) = C(33)	1.815(12)
Fe(4) - S(3)	2.285(4)	Fe(4) = S(4)	2.274(3)
Fe(4) - C(41)	1.797(13)	Fe(4) - C(42)	1.812(15)
Fe(4)-C(43)	1.814(12)	Fe(4)–C(44)	2.452(14)
O(11)~C(11)	1.141(16)	O(12)–C(12)	1.138(18)
O(13)-C(13)	1.136(14)	O(21)-C(21)	1.133(18)
O(22)-C(22)	1.137(16)	O(23)-C(23)	1.130(15)
O(24)-C(24)	1.281(16)	O(31)-C(31)	1.134(16)
O(32)-C(32)	1.142(18)	O(33)-C(33)	1.124(15)
O(41)–C(41)	1.134(16)	O(42) - C(42)	1.128(19)
O(43)C(43)	1.141(14)	O(44)–C(44)	1.196(17)
C(1) - C(2)	1.453(20)	C(1) - C(5)	1.463(19)
C(2)-C(3)	1.457(22)	C(3) - C(4)	1.358(15)
C(4)–C(5)	1.496(23)	C(6)-C(7)	1.433(20)
C(6) - C(10)	1.439(23)	C(7) - C(8)	1.399(21)
C(8)–C(9)	1.497(22)	C(9)-C(10)	1.447(19)

TABLE 4. Bond angles (°) for the cluster $CpRe(\mu-CO)(\mu_3-S)_2Fe_2(CO)_6$ (III)

Fe(1)-Re(1)-Fe(2)	75.3(1)	Fe(1)-Re(1)-S(1)	52.5(1)	S(1)-Fe(2)-C(22)	95.8(4)	S(2)-Fe(2)-C(22)	96.5(5)
Fe(2)-Re(1)-S(1)	53.2(1)	Fe(1) - Re(1) - S(2)	52.5(1)	C(21) - Fe(2) - C(22)	97.0(6)	Re(1)-Fe(2)-C(23)	111.8(5)
Fe(2)-Re(1)-S(2)	53.4(1)	S(1) - Re(1) - S(2)	80.7(1)	S(1)-Fe(2)-C(23)	167.1(5)	S(2)-Fe(2)-C(23)	90.5(5)
Fe(1)-Re(1)-C(1)	99.8(3)	Fe(2)-Re(1)-C(1)	149.7(4)	C(21)-Fe(2)-C(23)	93.9(6)	C(22)-Fe(2)-C(23)	96.2(6)
S(1) - Re(1) - C(1)	144.8(3)	S(2) - Re(1) - C(1)	99.5(4)	Re(1)-Fe(2)-C(24)	41.7(3)	S(1)-Fe(2)-C(24)	83.6(3)
Fe(1)-Re(1)-C(2)	81.1(3)	Fe(2)-Re(1)-C(2)	156.4(3)	S(2) - Fe(2) - C(24)	84.9(4)	C(21)-Fe(2)-C(24)	81.5(6)
S(1)-Re(1)-C(2)	110.3(4)	S(2) - Re(1) - C(2)	111.7(4)	C(22)-Fe(2)-C(24)	178.4(7)	C(23)-Fe(2)-C(24)	84.5(5)
C(1) - Re(1) - C(2)	36.7(5)	Fe(1)-Re(1)-C(3)	101.2(3)	Re(2)-Fe(3)-S(3)	55.0(1)	Re(2)-Fe(3)-S(4)	54.9(1)
Fe(2)-Re(1)-C(3)	148.5(4)	S(1) - Re(1) - C(3)	99.3(4)	S(3) - Fe(3) - S(4)	83.9(1)	Re(2)-Fe(3)-C(31)	146.9(4)
S(2) - Re(1) - C(3)	146.7(3)	C(1) - Re(1) - C(3)	61.6(5)	S(3) - Fe(3) - C(31)	103.4(4)	S(4) - Fe(3) - C(31)	102.3(4)
C(2) - Re(1) - C(3)	36.8(5)	Fe(1)-Re(1)-C(4)	135.9(3)	Re(2)-Fe(3)-C(32)	103.9(4)	S(3)-Fe(3)-C(32)	87.0(4)
Fe(2) - Re(1) - C(4)	141.8(4)	S(1) - Re(1) - C(4)	121.6(4)	S(4) - Fe(3) - C(32)	158.2(4)	C(31)-Fe(3)-C(32)	99.0(6)
S(2) - Re(1) - C(4)	157.2(4)	C(1) - Re(1) - C(4)	60.2(5)	Re(2)-Fe(3)-C(33)	103.6(4)	S(3)-Fe(3)-C(33)	157.7(4)
C(2) - Re(1) - C(4)	59.2(5)	C(3)-Re(1)-C(4)	35.1(4)	S(4) - Fe(3) - C(33)	88.3(5)	C(31)-Fe(3)-C(33)	98.7(5)
Fe(1)-Re(1)-C(5)	137.1(4)	Fe(2)-Re(1)-C(5)	138.3(3)	C(32)-Fe(3)-C(33)	92.8(6)	Re(2)-Fe(4)-S(3)	55.4(1)
S(1) - Re(1) - C(5)	160.5(4)	S(2) - Re(1) - C(5)	118.7(4)	Re(2)-Fe(4)-S(4)	55.4(1)	S(3) - Fe(4) - S(4)	83.4(1)
C(1) - Re(1) - C(5)	37.3(5)	C(2) - Re(1) - C(5)	63.0(5)	Re(2)-Fe(4)-C(41)	138.4(4)	S(3) - Fe(4) - C(41)	95.8(5)
C(3) - Re(1) - C(5)	64.0(5)	C(4) - Re(1) - C(5)	38.9(6)	S(4) - Fe(4) - C(41)	95.9(4)	Re(2)-Fe(4)-C(42)	112.2(4)
Fe(1)-Re(1)-C(24)	135.3(5)	Fe(2)-Re(1)-C(24)	60.0(5)	S(3) - Fe(4) - C(42)	167.6(4)	S(4) - Fe(4) - C(42)	89.8(4)
S(1)-Re(1)-C(24)	95.6(6)	S(2) - Re(1) - C(24)	97.2(5)	C(41)-Fe(4)-C(42)	95.2(6)	Re(2)-Fe(4)-C(43)	110.9(4)
C(1)-Re(1)-C(24)	119.0(6)	C(2)-Re(1)-C(24)	143.5(6)	S(3)-Fe(4)-C(43)	90.3(4)	S(4) - Fe(4) - C(43)	166.1(4)
C(3)-Re(1)-C(24)	115.8(6)	C(4) - Re(1) - C(24)	85.6(6)	C(41) - Fe(4) - C(43)	97.1(5)	C(42)-Fe(4)-C(43)	94.0(6)
C(5) - Re(1) - C(24)	83.9(6)	Fe(3)-Re(2)-Fe(4)	75.2(1)	Re(2)-Fe(4)-C(44)	43.2(3)	S(3) - Fe(4) - C(44)	86.0(4)
Fe(3) - Re(2) - S(3)	52.4(1)	Fe(4) - Re(2) - S(3)	53.4(1)	S(4) - Fe(4) - C(44)	84.6(3)	C(41)-Fe(4)-C(44)	178.1(5)
Fe(3)-Re(2)-S(4)	52.6(1)	Fe(4) - Re(2) - S(4)	53.1(1)	C(42) - Fe(4) - C(44)	83.0(6)	C(43) - Fe(4) - C(44)	82.6(5)
S(3) - Re(2) - S(4)	80.7(1)	Fe(3) - Re(2) - C(6)	80.8(3)	Re(1)-S(1)-Fe(1)	72.7(1)	Re(1)-S(1)-Fe(2)	71.4(1)
Fe(4)-Re(2)-C(6)	156.0(3)	S(3)-Re(2)-C(6)	110.4(4)	Fe(1)-S(1)-Fe(2)	93.6(1)	Re(1)-S(2)-Fe(1)	72.5(1)
S(4) - Re(2) - C(6)	111.3(3)	Fe(3)-Re(2)-C(7)	99.6(4)	Re(1)-S(2)-Fe(2)	71.0(1)	Fe(1)-S(2)-Fe(2)	93.3(1)
Fe(4) - Re(2) - C(7)	148.7(4)	S(3) - Re(2) - C(7)	98.6(4)	Re(2) - S(3) - Fe(3)	72.6(1)	Re(2)-S(3)-Fe(4)	71.2(1)
S(4)-Re(2)-C(7)	145.4(4)	C(6) - Re(2) - C(7)	36.3(5)	Fe(3) - S(3) - Fe(4)	93.4(1)	Re(2)-S(4)-Fe(3)	72.4(1)
Fe(3)-Re(2)-C(8)	135.4(3)	Fe(4)-Re(2)-C(8)	142.2(3)	Re(2)-S(4)-Fe(4)	71.5(1)	Fe(3) - S(4) - Fe(4)	93.4(1)
S(3)-Re(2)-C(8)	121.4(4)	S(4) - Re(2) - C(8)	157.4(4)	Re(1)-C(1)-C(2)	72.9(9)	Re(1)-C(1)-C(5)	70.8(9)
C(6) - Re(2) - C(8)	59.3(4)	C(7) - Re(2) - C(8)	36.1(5)	C(2)-C(1)-C(5)	111.3(14)	Re(1)-C(2)-C(1)	70.4(8)
Fe(3)-Re(2)-C(9)	136.6(3)	Fe(4)-Re(2)-C(9)	139.2(4)	Re(1)-C(2)-C(3)	70.1(8)	C(1)-C(2)-C(3)	107.4(11)
S(3) - Re(2) - C(9)	159.9(4)	S(4) - Re(2) - C(9)	119.2(4)	Re(1)-C(3)-C(2)	73.1(8)	Re(1) - C(3) - C(4)	69.7(7)
C(6) - Re(2) - C(9)	62.3(5)	C(7) - Re(2) - C(9)	64.0(6)	C(2)-C(3)-C(4)	105.8(12)	Re(1)-C(4)-C(3)	75.2(7)
C(8) - Re(2) - C(9)	38.5(5)	Fe(3)-Re(2)-C(10)	99.7(3)	Re(1)-C(4)-C(5)	72,7(7)	C(3)-C(4)-C(5)	115.8(12)
Fe(4)-Re(2)-C(10)	149.2(4)	S(3) - Re(2) - C(10)	144.9(4)	Re(1)-C(5)-C(1)	71.9(8)	Re(1)-C(5)-C(4)	68.4(7)
Fe(4) - Re(2) - C(44)	61.6(4)	S(3) - Re(2) - C(44)	98.5(4)	C(1)-C(5)-C(4)	99.7(11)	Re(2)-C(6)-C(7)	71.2(7)
S(4) - Re(2) - C(44)	96.5(4)	C(6) - Re(2) - C(44)	142.3(5)	Re(2)-C(6)-C(10)	70.2(7)	C(7)-C(6)-C(10)	109.1(12)
C(7) - Re(2) - C(44)	117.6(5)	C(8) - Re(2) - C(44)	85.3(5)	Re(2)-C(7)-C(6)	72.4(8)	Re(2) - C(7) - C(8)	69.4(8)
C(9) - Re(2) - C(44)	82.3(5)	C(10) - Re(2) - C(44)	116.2(5)	C(8)-C(9)-C(10)	100.2(13)	Re(2)-C(10)-C(6)	73.2(7)
Re(1)-Fe(1)-S(1)	54.8(1)	Re(1)-Fe(1)-S(2)	55.1(1)	Re(2)-C(10)-C(9)	73.1(7)	C(6) - C(10) - C(9)	111.4(13)
S(1)-Fe(1)-S(2)	83.8(1)	Re(1)-Fe(1)-C(11)	145.0(4)	Fe(1)-C(11)-O(11)	177.9(11)	Fe(1)-C(12)-O(12)	180.0(16)
S(1)-Fe(1)-C(11)	101.4(5)	S(2)-Fe(1)-C(11)	101.6(4)	Fe(1)-C(13)-O(13)	177.3(12)	Fe(2)-C(21)-O(21)	178.1(10)
Re(1)-Fe(1)-C(12)	105.1(4)	S(1) - Fe(1) - C(12)	158.9(4)	Fe(2)-C(22)-O(22)	177.4(12)	Fe(2)-C(23)-O(23)	178.3(14)
S(2) - Fe(1) - C(12)	88.7(4)	C(11)-Fe(1)-C(12)	99.4(6)	Re(1)-C(24)-Fe(2)	78.3(5)	Re(1)-C(24)-O(24)	160.2(14)
Re(1)-Fe(1)-C(13)	104.8(4)	S(1) - Fe(1) - C(13)	88.6(4)	Fe(2)-C(24)-O(24)	120.8(11)	Fe(3)-C(31)-O(31)	178.9(11)
S(2)-Fe(1)-C(13)	159.0(4)	C(11)-Fe(1)-C(13)	99.1(5)	Fe(3)-C(32)-O(32)	176.5(13)	Fe(3)-C(33)-O(33)	177.9(12)
C(12)-Fe(1)-C(13)	91.5(6)	Re(1)-Fe(2)-S(1)	55.4(1)	Fe(4) - C(41) - O(41)	179.8(15)	Fe(4)-C(42)-O(42)	176.6(12)
Re(1)-Fe(2)-S(2)	55.6(1)	S(1) - Fe(2) - S(2)	83.5(1)	Fe(4) - C(43) - O(43)	179.0(9)	Re(2)-C(44)-Fe(4)	75,2(5)
Re(1)-Fe(2)-C(21)	109.8(4)	S(1)-Fe(2)-C(21)	89.3(4)	Re(2)-C(44)-O(44)	162.6(11)	Fe(4) - C(44) - O(44)	122.1(9)
S(2)-Fe(2)-C(21)	165.3(4)	Re(1)-Fe(2)-C(22)	138.9(4)				

also by interaction of $S_2 Fe_2(CO)_6$ (I) with $(Ph_3P)_2 Pt-(C_2H_4)$ [5] or with $(Ph_3P)_4 Pt$ (in the presence of methyl iodide, which scavenges the triphenylphosphine eliminated) [3]:

$$S_{2}Fe_{3}(CO)_{9} + (Ph_{3}P)_{2}PtCl_{2}$$

$$S_{2}Fe_{2}(CO)_{6}^{2-} + (Ph_{3}P)_{2}PtCl_{2}$$

$$S_{2}Fe_{2}(CO)_{6} + (Ph_{3}P)_{2}Pt(C_{2}H_{4})$$

$$S_{2}Fe_{2}(CO)_{6} + (Ph_{3}P)_{4}Pt + Mel$$

$$\begin{array}{c}
 Ph_{3}P \\
 Ph_{3}P
\end{array} Pt \\
 S \\
 S \\
 Fe(CO)_{3} \\
 Fe(CO)_{3}
\end{array}$$
(II)

The structure of II was solved by X-ray analysis (Fig. 1, Tables 1 and 2). It was found to be similar to the Pd-containing cluster [2]. Pt^{II} and Pd^{II} ions have a typical square-planar ligand environment with practically the same M-S bond lengths (Pt- S_{av} , 2.33(1), Pd-S_{av} 2.32(1) Å [2]), although Pt-P bonds (mean 2.29(1) Å) are slightly shorter than Pd–P bonds (mean 2.33(1) Å [2]). Geometry of the $S_2Fe_2(CO)_6$ fragment is practically the same in both clusters (in II, Fe-Fe_{av.} and Fe-S_{av.} bond lengths are 2.496(7) and 2.29(1) Å respectively for 4 independent molecules in the cell). Pt ··· Fe distances are more than 3.3 Å and are evidently nonbonding. The transmetallation reaction gives along with II a more soluble black-brown crystalline product, probably (Ph₃P)(CO)PtS₂Fe₂(CO)₆. Its IR spectrum, in comparison with that of II has less intense bands of phenyl groups in the region of 680 and 730 cm⁻¹, and also a supplementary ν (CO) band at 2055 cm⁻¹. However, the yield of this substance was not sufficient for elemental analysis.

It is possible that transmetallation of $S_2Fe_3(CO)_9$ begins with coordination of $(Ph_3P)_2PtCI_2$ to the μ_3 -S bridge, by analogy with W(CO)₅ fragment coordination to the bridge atom in the $(CO)_4W(\mu_3-S)_2Fe_2(CO)_6$ cluster [2]. The absence of reaction between $(Ph_3P)_2PtCI_2$ and $(\mu_3-NPh)_2Fe_3(CO)_9$ [6] even in boiling toluene or in THF under UV-irradiation could be explained by the impossibility of $(Ph_3P)_2PtCI_2$ coordination with phenylnitrene bridges, as they have no lone pairs. The absence of direct Pt-Fe bonds in **H** is in accordance with the stable 16e⁻⁻ configuration of Pt^{II} in the square-planar ligand environment. It means that the $S_2Fe_2(CO)_6$ fragment plays the role of a 2e⁻⁻ donor with retention of the Fe-Fe bond.

Another situation arises in the reaction of $S_2Fe_2(CO)_6$ (I) with $CpRe(CO)_2(THF)$ (generated under UV light) which gives the $CpRe(\mu-CO)(\mu_3-S)_2Fe_2(CO)_6$ (III) cluster (Fig. 2, Tables 3 and 4):



(III)

At the elimination of the CO and tetrahydrofuran molecules the 4e⁻ deficient CpRe(CO) fragment formally arises. This deficit is compensated by coordination of I as a 4e⁻ donor with breaking of the Fe-Fe bond and with formation of two Re-S (mean 2.344(3) \hat{A}) and two Re-Fe bonds (mean 2.712(2) \hat{A}). In addition the semibridge carbonyl group appears between the Re atom and one of the Fe atoms, showing a band at 1840 cm⁻¹ in IR spectrum. The Fe₂S₂ cycle is nearly planar having a dihedral angle of 153.3° between Fe₅S planes. This angle is close to 156° for the previously studied Me₅C₅Co(μ_3 -S)₂Fe₂(CO)₆ cluster, whose MO calculation corresponds to formation of $S \rightarrow Co$ and $Co \rightarrow Fe$ bonds [3]. Probably the same type of bonding occurs for III with formation of $S \rightarrow Re$ and $Re \rightarrow Fe$ bonds being supplemented by dative Fe-CO_{bridge} interaction. This new type of coordination of $S_2 Fe_2(CO)_6$ (as a formal 6e donor) contrasts to the earlier observed type in the CpV(O)(μ_3 -S), Fe₃(CO)₆ cluster, which retains as a Fe-Fe bond and contains two Fe \rightarrow V bonds [2].

TABLE 5. Crystallographic data for the clusters $(Ph_3P)_2Pt(\mu_3, S)_2Fe_2(CO)_6$ (II) and $CpRe(\mu-CO)(\mu_3-S)_2Fe_2(CO)_4$ (III)

	11	III
Crystal system	monoclinic	triclinic
Space group	$P2_1 \neq c$	$P\bar{1}$
a (Å)	24.885(9)	9.272(2)
<i>b</i> (Å)	19,770(8)	9.452(3)
c (Å)	34.085(12)	19.936(7)
α ([^])		80.45(2)
β(*)	90.55(1)	89.63(3)
γ (°)		74,43(2)
$V(\text{\AA}^3)$	16768(18)	1658.4(1.2)
Z	16	4
Number of reflections	10897	6895
measured		
Number of independent		
reflections with		
$l > 6\sigma(1)$	8564	
$I \ge 2\sigma(I)$		4525
R	0.080	0.043
R _w	0.077	0.043

3. Experimental details

All operations connected with syntheses of both initial and final products were performed in a flow of

pure dry argon in absolute solvents. The initial complexes $(NPh)_2Fe_3(CO)_9$ [6], $S_2Fe_2(CO)_6$, $S_2Fe_3(CO)_9$ [7] and $CpRe(CO)_3$ [8] were synthesized by published procedures. The IR spectra were recorded in KBr

TABLE 6. Atomic coordinates (×10⁴) for the cluster (Ph₃P)₂Pt(μ_3 -S)₂Fe₂(CO)₆ (II)

Atom	x	у	z	Atom	x	у	z
Pt(1)	1896(1)	3151(1)	4912(1)	C(13)	788(17)	1342(16)	4482(9)
Pt(2)	5505(1)	1866(1)	2656(1)	C(21)	1094(12)	2615(16)	5763(9)
Pt(3)	- 3056(1)	1850(1)	5066(1)	C(22)	142(14)	2549(18)	5336(10)
Pt(4)	593(1)	510(1)	2449(1)	C(23)	713(12)	1425(16)	5375(9)
Fe(1)	892(2)	2221(3)	4558(1)	C(31)	6653(17)	335(21)	3347(14)
Fe(2)	822(2)	2301(3)	5283(1)	C(32)	6077(14)	1369(15)	3581(11)
Fe(3)	6487(2)	1168(3)	3186(2)	C(33)	7098(17)	1596(16)	3359(10)
Fe(4)	6635(2)	998(3)	2468(2)	C(41)	6458(14)	1135(22)	1984(13)
Fe(5)	-4104(2)	2765(3)	4727(2)	C(42)	7340(14)	1182(17)	2420(15)
Fe(6)	- 4149(2)	2609(3)	5456(2)	C(43)	6763(15)	135(19)	2454(12)
Fe(7)	1650(2)	1325(3)	2058(2)	C(51)	- 3754(14)	2796(17)	4310(12)
Fe(8)	1650(2)	1359(3)	2790(2)	C(52)	-4321(15)	3609(16)	4758(12)
S(1)	968(3)	3222(5)	4893(3)	C(53)	- 4719(14)	2434(26)	4613(10)
S(2)	1607(3)	2040(5)	4977(3)	C(61)	- 4809(15)	2398(19)	5472(9)
S(3)	5838(4)	760(5)	2771(3)	C(62)	- 4261(16)	3405(20)	5611(11)
S(4)	6424(3)	2011(4)	2747(3)	C(63)	- 3940(22)	2207(24)	5886(13)
S(5)	- 3376(4)	2945(5)	5134(3)	C(71)	2325(16)	1120(25)	1969(12)
S(6)	- 3980(4)	1751(5)	5028(3)	C(72)	1370(18)	1003(19)	1633(10)
S(7)	909(3)	1641(5)	2411(3)	C(73)	1752(18)	2138(22)	2000(18)
S(8)	1523(3)	386(5)	2448(3)	C(81)	1773(12)	2287(18)	2904(9)
P (1)	2782(4)	2820(5)	2954(3)	C(82)	1364(13)	1137(18)	3251(10)
P(2)	2044(4)	4279(5)	4834(3)	C(83)	2349(13)	1059(22)	2895(13)
P(3)	4627(4)	1476(5)	2606(3)	C(101)	2980(12)	2278(15)	4563(9)
P(4)	5343(4)	3003(4)	2563(2)	C(102)	3538(16)	2161(20)	4469(12)
P(5)	-2177(4)	2230(5)	5131(3)	C(103)	3704(15)	1817(21)	4160(12)
P(6)	- 2901(4)	718(5)	5039(3)	C(104)	3299(15)	1506(19)	3889(11)
P(7)	433(4)	-609(5)	2484(3)	C(105)	2764(14)	1623(18)	3990(10)
P(8)	-282(3)	851(5)	2418(3)	C(106)	2589(13)	2017(17)	4297(10)
O(11)	1418(10)	2502(16)	3838(6)	C(107)	2863(13)	2291(17)	5428(9)
O(12)	-201(10)	2609(21)	4379(8)	C(108)	2547(12)	2473(16)	5707(9)
O(13)	689(12)	808(12)	4436(8)	C(109)	2656(16)	2148(21)	6069(12)
O(21)	1271(12)	2692(16)	6058(7)	C(110)	3013(17)	1613(22)	6121(12)
O(22)	- 311(9)	2712(10)	5348(6)	C(111)	3280(17)	1397(22)	5754(14)
O(23)	604(10)	881(15)	5432(8)	C(112)	3200(15)	1771(20)	5415(11)
O(31)	6776(18)	- 239(19)	3424(12)	C(113)	3318(15)	3403(19)	5046(11)
O(32)	5827(12)	1471(18)	3860(7)	C(114)	3541(15)	3760(19)	4654(11)
O(33)	7476(10)	1861(16)	3446(8)	C(115)	3957(18)	4243(23)	4689(13)
O(41)	6332(11)	1339(17)	1666(7)	C(116)	4239(19)	4266(26)	5134(15)
O(42)	7764(10)	1376(15)	2420(10)	C(117)	4045(18)	3909(24)	5442(13)
O(43)	6867(14)	- 403(16)	2423(13)	C(118)	3590(17)	3455(22)	5385(12)
O(51)	- 3585(10)	2845(15)	3987(8)	C(201)	2443(15)	4497(22)	4364(11)
O(52)	- 4442(12)	4162(14)	4753(12)	C(202)	2618(19)	5264(26)	4328(14)
O(53)	- 5128(11)	2176(21)	4475(10)	C(203)	2870(19)	5184(26)	3880(15)
O(61)	- 5273(11)	2236(15)	5444(8)	C(204)	2873(20)	4640(30)	3659(15)
O(42)	4318(14)	3954(17)	5750(10)	C(205)	2652(21)	4053(29)	3739(16)
O(63)	- 3801(12)	1929(20)	6180(8)	C(206)	2393(16)	3952(21)	4116(12)
O(71)	2755(10)	918(22)	1907(8)	C(207)	1455(14)	4769(19)	4783(11)
O(72)	1210(11)	838(16)	1323(9)	C(208)	1156(18)	4732(23)	4375(13)
O(73)	1846(11)	2689(14)	1919(8)	C(209)	672(20)	5103(26)	4336(14)
O(81)	1862(12)	2802(13)	2960(8)	C(210)	494(15)	5512(20)	4659(12)
O(82)	1132(9)	1013(12)	3520(7)	C(211)	690(21)	5425(26)	5082(15)
O(83)	2770(10)	922(15)	2937(9)	C(212)	1225(17)	5097(22)	5040(12)
C (11)	1202(16)	2410(16)	4142(12)	C(213)	2377(11)	4677(15)	5242(8)
C(12)	227(14)	2394(27)	4471(13)	C(214)	2223(15)	4425(21)	5618(12)

TABLE 6. (continued)

Atom	X	y	2	Atom	X	X	2
C(215)	2514(25)	4747(32)	5977(17)	C(517)	-1324(17)	3312(23)	4321(14)
C(216)	2909(17)	5213(23)	5964(13)	C(518)	-1421(16)	3002(21)	4663(12)
C(217)	3040(21)	5383(27)	5616(17)	C(601)	3483(13)	163(17)	4963(10)
C(218)	2845(16)	5039(21)	5217(12)	C(602)	- 3735(15)	- 255(19)	5174(11)
C(301)	4560(14)	981(18)	2146(10)	C(603)	4206(12)	575(15)	5095(9)
C(302)	4984(15)	795(19)	1942(11)	C(604)	- 4509(20)	-508(26)	4834(15)
C(303)	4937(17)	416(21)	1568(12)	C(605)	- 4256(14)	3(18)	4487(10)
C(304)	4423(19)	288(23)	1401(13)	C(606)	-3760(17)	355(21)	4554(12)
C(305)	3965(23)	472(29)	1634(18)	C(607)	-2636(13)	428(16)	5497(9)
C(306)	4015(18)	785(23)	2000(14)	C(608)	- 2149(13)	106(17)	5516(10)
C(307)	4510(12)	893(16)	3044(9)	C(609)	-1917(17)	-6(22)	5943(13)
C(308)	4716(13)	1102(18)	3372(10)	C(610)	2260(18)	140(22)	6248(12)
C(309)	4641(14)	710(19)	3728(10)	C(611)	-2742(16)	429(21)	6233(11)
C(310)	4338(16)	119(22)	3666(12)	C(612)	-2928(14)	637(18)	5818(10)
C(311)	4094(15)	~ 86(20)	3302(12)	C(613)	-2447(12)	393(16)	4642(9)
C(312)	4180(13)	352(17)	2969(10)	C(614)	- 2329(14)	-294(18)	4638(10)
C(313)	4027(13)	2060(18)	2591(11)	C(615)	-2018(17)	- 506(22)	4305(13)
C(314)	3858(21)	2354(26)	2296(15)	C(616)	- 1832(21)	- 156(29)	4015(16)
C(315)	3431(19)	2818(23)	2304(13)	C(617)	-2004(19)	569(27)	4015(14)
C(316)	3169(16)	2902(21)	2603(13)	C(618)	-2325(14)	808(19)	4329(11)
C(317)	3349(17)	2523(23)	2952(13)	C(701)	36(12)	-890(17)	29()2(9)
C(318)	3802(14)	2139(18)	2960(10)	C(702)	-177(16)	-1567(21)	2921(12)
C(401)	5045(13)	3223(20)	2099(10)	C(703)	-480(15)	-1750(20)	3249(11)
C(402)	4983(14)	2698(19)	1824(11)	C(704)	-556(16)	-1277(23)	3541(12)
C(403)	4751(21)	2863(28)	1418(16)	C(705)	+330(17)	- 625(23)	3567(12)
C(404)	4595(17)	3534(25)	1374(13)	C(706)	- 26(17)	- 397(23)	3202(13)
C(405)	4631(18)	4110(25)	1671(14)	C(707)	133(17)	-924(21)	2004(12)
C(406)	4850(16)	3897(21)	2050(12)	C(708)	431(18)	~665(24)	1673(14)
C(407)	5954(15)	3354(20)	2534(11)	C(709)	141(20)	- 874(25)	1312(14)
C(408)	6103(19)	3909(24)	2812(13)	C(710)	31 /(18)	1303(22)	1294(13)
C(409)	6666(23)	4146(28)	2828(16)	C(711)	- 582(17)	~ (5)2(22)	1643(13)
C(410)	6922(22)	4056(28)	2539(18)	C(712)	- 377(16)	-1331(21)	2016(12)
C(411)	6783(21)	3825(26)	2196(16)	C(713)	1041(15)	- 1086(19)	2560(11)
C(412)	6277(20)	3426(25)	22(0(14)	C(714)	12.30(15)	~~ 1621(19)	2244(11)
C(413)	4946(16)	33(0)(22)	2968(12)	0(715)	170.5(14)		2314(10)
C(414)	44/9(14)	3768(18)	2875(10)	C(716)	1940(18)	- 1891(26)	2/02(14)
C(415)	4194(25)	3934(33)	3243(21)	CV7127	1700(10)	- 1472(23)	2950(15)
C(415)	4358(24)	3739(30)	(01)69666	C(201)	242(12)	- 1078(20)	2951(11)
C(417)	4014(2.)	3147(20)	3720(16)	C(801)	= -702(1.1)	(45/(17)	2014(2)
C(416)		2748(20)	5507(11)	C(802)		2381(21)	1639(12)
C(502)	= 2104(10) = 1763(16)	2746(20)	5597(11)	C(803)	= .176(15)	2246(20)	1320(11)
C(502)	= 1703(10) = 1733(10)	3255(22)	6037(15)	C(805)	- 100(16)	1611(21)	$1.3 \pm 0(1.1)$ $1.3 \pm 0(1.1)$
C(504)	2057(23)	3364(29)	6298(16)	C(805)	- 39(12)	1312(16)	1682(10)
C(505)		2872(26)	6238(15)	C(807)	- 505(12)	1249(16)	2844(9)
C(506)	= 2484(14)	2566(18)	5880(11)	C(808)	= 1048(14)	1110(18)	2044(7)
C(507)	-1582(17)	1663(22)	5235(14)	C(809)	1171(15)	1743(20)	3286(12)
C(508)	-1426(23)	1577(28)	5575(17)	C(810)	-786(19)	2025(24)	3513(13)
C(509)	-862(22)	1016(29)	5550(17)	C(811)	-233(19)	1941(26)	3428(14)
C(510)	-786(17)	840(23)	5193(15)	C(812)	-86(14)	1558(19)	3129(11)
C(511)	- 882(39)	985(50)	4741(29)	C(813)	- 847(14)	338(18)	2308(10)
C(512)	- 1375(21)	1396(26)	4869(16)	C(814)	-1090(18)	-100(23)	2623(13)
C(513)	-1997(16)	2743(20)	4697(11)	C(815)	- 1537(13)	-520(18)	2581(10)
C(514)	-2375(16)	2877(20)	4435(12)	C(816)	-1725(18)	- 497(24)	2205(14)
C(515)	-2246(19)	3219(25)	4046(13)	C(817)	1527(19)	-198(25)	1885(14)
C(516)	- 1692(21)	3453(25)	4023(14)	C(818)	- 1052(13)	313(17)	1931(10)

pellets with a Specord 75 IR instrument. The X-ray diffraction data for II (at 20°C) and III (at -100° C) were collected with Syntex P2₁ and Siemens P3/PC automatic diffractometers, respectively (λ (Mo-K α), θ -2 θ scan, $2\theta_{max}$ 60°). Crystallographic data are listed

TABLE 7. Atomic coordinates (×10⁴) and equivalent isotropic displacement coefficients (Å²×10³) for the cluster CpRe(μ -CO)(μ_{3} -S)₂Fe₂(CO)₆ (III)

Atom	x	у	z	U _{eq} ^a
Re(1)	- 2679(1)	10737(1)	9201(1)	19(1)
Re(2)	- 2295(1)	9223(1)	4302(1)	19(1)
Fe(1)	- 3086(2)	12398(2)	7921(1)	20(1)
Fe(2)	- 2130(2)	8714(2)	8359(1)	19(1)
Fe(3)	- 1929(2)	7639(2)	3258(1)	20(1)
Fe(4)	- 2847(2)	11303(2)	3165(1)	17(1)
S(1)	- 4261(3)	10616(3)	8314(1)	19(1)
S(2)	- 974(3)	10582(3)	8319(1)	19(1)
S(3)	- 4013(3)	9445(3)	3408(1)	19(1)
S(4)	- 727(3)	9388(3)	3385(1)	19(1)
O(11)	- 3055(10)	12326(11)	6446(4)	35(4)
O(12)	- 1408(11)	14614(10)	7951(5)	38(4)
O(13)	- 5942(11)	14672(10)	7965(5)	39(4)
O(21)	- 3929(12)	6589(10)	8717(6)	46(4)
O(22)	- 2157(11)	8618(11)	6897(5)	40(4)
O(23)	746(12)	6426(11)	8710(6)	50(4)
O(24)	- 1811(12)	7531(9)	9983(4)	40(4)
O(31)	- 1948(11)	7710(10)	1773(5)	36(4)
O(32)	- 3694(11)	5507(10)	3668(5)	39(4)
O(33)	913(12)	5349(10)	3645(5)	42(4)
O(41)	- 2915(11)	11426(11)	1686(5)	39(4)
O(42)	- 1011(12)	13409(10)	3124(6)	45(4)
O(43)	- 5738(11)	13549(10)	3225(5)	38(4)
O(44)	- 3034(11)	12392(10)	4634(5)	37(4)
C(1)	- 1864(17)	12303(15)	9776(7)	35(6)
C(2)	- 3356(17)	13103(15)	9493(7)	36(6)
C(3)	- 4380(16)	12258(13)	9785(6)	29(5)
C(4)	- 3528(16)	11075(13)	10221(6)	31(5)
C(5)	- 1885(19)	10950(16)	10249(6)	38(6)
C(6)	-1701(16)	6845(13)	4925(6)	30(5)
C(7)	- 3156(19)	7645(15)	5102(7)	42(6)
C(8)	- 2910(16)	8826(12)	5384(5)	26(5)
C(9)	- 1312(17)	8879(15)	5395(5)	38(6)
C(10)	- 622(17)	7601(14)	5081(6)	35(5)
C(11)	- 3056(14)	12326(14)	7019(6)	26(5)
C(22)	- 2120(15)	8671(13)	7462(6)	28(5)
C(23)	- 344(16)	7319(13)	8575(7)	31(5)
C(24)	- 2201(18)	8745(16)	9552(8)	51(7)
C(31)	- 1942(14)	7697(13)	2343(7)	23(5)
C(32)	- 3014(16)	6332(13)	3488(7)	29(5)
C(33)	- 168(16)	6225(14)	3484(6)	28(5)
C(41)	- 2891(16)	11379(13)	2258(6)	28(5)
C(42)	- 1740(15)	12620(14)	3155(7)	28(5)
C(43)	- 4616(15)	12688(12)	3205(6)	24(5)
C(44)	-2758(15)	11271(14)	4396(7)	34(5)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ii} tensor.

in Table 5. The structures were solved by the direct method and refined in full-matrix anisotropic approximation for all non-hydrogen atoms. Atomic coordinates are listed in Tables 6 and 7. All calculations were performed with the Siemens SHELXTL PLUS program package (PC version).

3.1. $(Ph_3P)_2Pt(\mu_3-S)_2Fe_2(CO)_6$ (II)

A solution of 0.32 g (0.40 mmol) of (Ph₃P)₂PtCl₂ in 20 ml CH₂Cl₂ and 15 ml toluene was doubly concentrated in vacuo, until precipitation began. 0.20 g (0.40 mmol) of $S_2Fe_3(CO)_9$ was then added and the mixture was heated at 95°C for 10 h. The solution was filtered and the black solid deposited on the flask and chromatographed on SiO₂. The unreacted $S_2Fe_3(CO)_9$ and the brown band (A) were eluted by benzene/heptane 1:3 mixture. The orange band (B) was then eluted by benzene. The solution of (B) gave on cooling thin orange needles II insoluble in heptane. Single crystals for X-ray structural analysis were obtained by crystallization from CH₂Cl₂/ether/heptane mixture. Yield 0.05 g (11.5%). IR spectra (ν , cm⁻¹): 510s, 530w, 560s, 605m, 680w, 730m, 990vw, 1050vw, 1080m, 1145vw, 1170vw, 1420m, 1465w, 1935vs, 1960vs, 1990vs, 2030vs.

The solution of (A) was concentrated *in vacuo* and after cooling black crystalline needles were formed. These are easily soluble even in pentane but the quantity of crystals was not sufficient for elemental analysis. IR spectra (ν , cm⁻¹): 505s, 560w, 680s, 733m, 990m, 1075m, 1150vw, 1175vw, 1420m, 1469m, 1940–2020vs multiplet, 2055vs.

3.2. $CpRe(\mu - CO)(\mu_3 - S)_2 Fe_2(CO)_6$ (III)

The colourless solution of 0.46 g (1.37 mmol) of CpRe(CO)₃ in 25 ml of THF was irradiated by UV light (PRK-4 lamp) in a quartz Schlenk vessel at room temperature for 7 h. 0.24 g (0.70 mmol) of $S_2Fe_2(CO)_6$ was added to the yellow solution of CpRe(CO)₂(THF) and the mixture was stirred at 20°C without UV-irradiation. After 12 h $S_2Fe_2(CO)_6$ disappeared (TLC data) and the solution was a brown colour. The mixture was evaporated to dryness *in vacuo* and the precipitate was extracted by hexane. The solution was concentrated and after cooling black-brown rhombic crystals of III were formed (yield 0.18 g, 41.2%). IR spectra (ν , cm⁻¹): 425m, 455s, 480vw, 492vw, 540vs, 590vs, 825m, 835vw, 1005w, 1050w, 1400w, 1840vs, 1952–2068vs multiplet, 3080 wbr.

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