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THE REACTION OF PhSR(R = Fc OR Ph) WITH $Ru_3(CO)_{12}$*

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Abstract—The reaction of SPh_2 with $Ru_3(CO)_{12}$ affords $(\mu\text{-SR})(\mu\text{-}\eta^1;\ \eta^6\text{-}C_6H_5)Ru_3(CO)_8$ (Ru–Ru), R = Ph; **7** in 70% yield. Compound **7** results from S—Ph cleavage and no products of orthometallation reactions are observed. Similarly, SFcPh (**6**) and $Ru_3(CO)_{12}$ afford **8** (R = Fc) in good yield in addition to smaller amounts of $(\mu\text{-SFc})_4Ru_3(CO)_7$ (3Ru—Ru)·$2CHCl_3$ (**9**) and $(\mu_4\text{-S})(\mu\text{-SFc})_6Ru_4(CO)_8$ (**10**). Crystals of **6** are orthorhombic, space group $P2_12_12_1$, $a = 9.014(2)$ Å, $b = 20.032(2)$ Å, $c = 7.313(2)$ Å, $Z = 4$; those of **7** are orthorhombic, space group $P2_12_12_1$, $a = 13.733(4)$ Å, $b = 19.886(2)$ Å, $c = 8.140(3)$ Å, $Z = 4$; those of **9** are monoclinic, space group $P2_1/n$, $a = 16.942(2)$ Å, $b = 17.874(2)$ Å, $c = 19.538(3)$ Å, $\beta = 105.77(1)°$, $Z = 4$; and those of **10** are monoclinic, space group $C2/c$, $a = 12.524(2)$ Å, $b = 24.202(3)$ Å, $c = 22.991(2)$ Å, $\beta = 95.32(2)°$, $Z = 4$. The structures were solved by Patterson (**6** and **7**) or direct methods (**9** and **10**) and were refined by full-matrix least-squares procedures to $R = 0.029$, 0.025, 0.035 and 0.035 for 1499, 3144, 5154 and 3882 reflections with $I \geqslant 3\sigma(I)$, respectively.

The pyrolysis of arylphosphine or arsine derivatives of $M_3(CO)_{12}$ (M = Ru, Os) affords many derivatives that result from an initial cluster assisted orthometallation of the aryl ring; often, further reaction results in P(As)—C cleavage and the formation of aryne complexes.[1–4] Alternatively, the derivatives can be prepared by simply heating $M_3(CO)_{12}$ with the appropriate phosphine or arsine. Some of these reactions occur under surprisingly mild conditions. A typical product from $Os_3(CO)_{12}$ and PPh_3 is the benzyne derivative **1**.[1] Less typical are the ferrocyne,[2] benzynechromium tricarbonyl[3] and naphthyne derivatives,[4] **2–4**.

The related reactions of sulphides with $M_3(CO)_{12}$ have not received much attention, although pyrolysis of $Os_3(CO)_{12}$ with SMePh affords the benzyne complex **5** in low yield.[5] The present paper describes some of our studies involving $Ru_3(CO)_{12}$ and the sulphides SPh_2 and SFcPh [FcH = $Fe(\eta^5\text{-}C_5H_5)_2$]. The crystal structure of SFcPh (**6**) and three reaction products **7**, **9** and **10**, which involve S—Ph cleavage, are described.

EXPERIMENTAL

The methodology used in this study was essentially the same as described previously.[2–5] Diphenylsulphide was purchased from K and K Laboratories Inc. Ferrocenylphenylsulphide (**6**) was prepared as described by Rausch.[6] We also isolated $Fe(\eta^5\text{-}C_5H_4SPh)_2$ from the same reaction (10% yield) because of the production of the dilithiated intermediate in the initial lithiation reaction. The identity of the 1,1′-derivative was confirmed by comparison with an authentic sample.[7]

Pyrolysis of $Ru_3(CO)_{12}$ *with* SPh_2

A solution of $Ru_3(CO)_{12}$ (192 mg, 0.30 mmol) and SPh_2 (1 cm^3, excess) in toluene (25 cm^3) was refluxed for 15 h. TLC revealed the formation of one major and two minor products. The solvent was removed *in vacuo*, and the residue was chromatographed on alumina with 3 : 1 petroleum ether–CH_2Cl_2 as eluent. The first orange band

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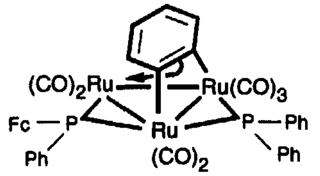
* Dedicated to Professor E. W. Abel, on the occasion of his retirement.

† Author to whom correspondence should be addressed.



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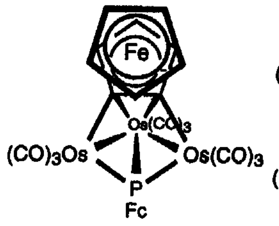

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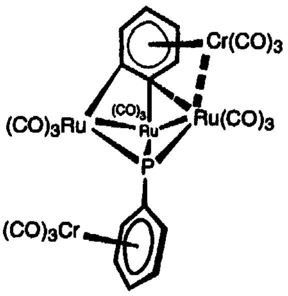

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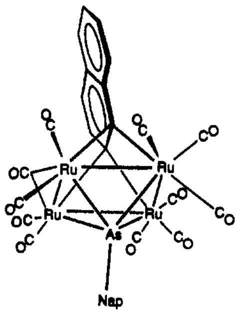

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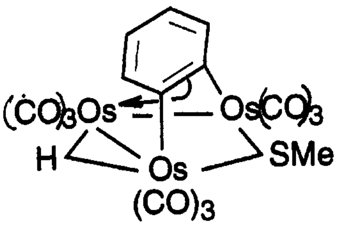


5

(15%) has not been characterized. The second major band contained complex **7**, which was obtained as a yellow solid in 70% yield. ^{1}H NMR (300 MHz): δ 7.41 (m, 2H), 7.23–7.08 (m, 3H), 6.58 (tm, 1H), 6.00 (m, 2H), 5.34 (tm, 1H), 4.70 (dm, 1H). Mass spectrum (FAB): *m/z* 715 (P$^+$), 687, 659, 630 (base peak), 601, 574, 548, 519, 490. Found: C, 33.3; H. 1.5. Calc. for $C_{20}H_{10}O_8Ru_3S$: C, 33.7; H, 1.4%.

Pyrolysis of $Ru_3(CO)_{12}$ *with* SFcPh

A solution of $Ru_3(CO)_{12}$ (250 mg, 0.39 mmol) and SFcPh (100 mg, 0.34 mmol) in toluene (50 cm^3) was refluxed for 11 h. The solution changed colour from orange to dark red in 15 min and to dark brown in 50 min. TLC revealed the presence of three major products. The solvent was removed *in vacuo* and the residue was chromatographed on silica with 3 : 1 petroleum ether–CH_2Cl_2 as eluent. The first band (25%) contained a mixture of two complexes **9** and **10** that were separated by TLC. Recrystallization from $CHCl_3$ gave crystals of **9** and **10**. The second yellow band contained **8** (55%). The third band (10%) contained an unidentified orange solid.

Compound **8**, yellow solid, ^{1}H NMR (200 MHz): δ 6.57 (m, 1H, Ph), 6.05 (m, 2H, Ph), 5.28 (m, 1H, Ph), 4.65 (m, 1H, Ph), 4.41 (m, 1H), 4.24 (m, 1H), 4.21 (s, 5H), 4.14 (m, 1H), 4.07 (m, 1H). Mass spectrum (FAB): *m/z* 823 (P$^+$), 794, 767, 739, 710, 683, 654, 626, 597 (broad, base peak), 532, 521. Found: C, 35.2; H, 1.98. Calc. for $C_{24}H_{14}FeO_8Ru_3S$: C, 35.1; H, 1.7%.

The third band was an orange solid. ^{1}H NMR (200 MHz): δ 7.25–7.10 (m), 7.08–7.00 (m), 6.88–6.78 (m), 4.38 (m), 4.33 (m), 4.25 (s), 4.17–4.07 (m), 3.90–3.80 (m), 3.80–3.50 (very broad m), 3.12 (m), 2.93 (m).

X-ray crystallographic analyses of **7**, **9**, **10** *and* SFcPh (**6**)

Crystallographic data appear in Table 1. The final unit-cell parameters were obtained by least-squares on the setting angles for 25 reflections with $2\theta = 28.1$–$38.9°$ for **6**, 41.6–50.1° for **7**, 20.4–27.6° for **9** and 10.6–20.3° for **10**. The intensities of three standard reflections, measured every 200 reflections throughout the data collections, showed only small random fluctuations for all four complexes. The data were processed[8] and corrected for Lorentz and polarization effects and absorption (empirical, based on azimuthal scans for three reflections).

The structures were solved by Patterson (**6** and **7**) or direct (**9** and **10**) methods. For **10** where there was a choice between a centrosymmetric and a non-centrosymmetric space group, the structure analysis

Table 1. Crystallographic data[a]

Compound	FcSPh (**6**)	$(\mu\text{-SPh})(\mu\text{-}\eta^1;\eta^6\text{-}C_6H_5)Ru_3(CO)_8$ (M—M) ; (**7**)	$(\mu\text{-SFc})_4Ru_3(CO)_7$(3M—M)·2 $CHCl_3$ (**9**)	$(\mu_4\text{-S})(\mu\text{-SFc})_6Ru_4(CO)_8$ (**10**)
Formula	$C_{16}H_{14}FeS$	$C_{20}H_{10}O_8Ru_3S$	$C_{47}H_{36}Fe_4O_7Ru_3S_4\cdot 2CHCl_3$	$C_{68}H_{54}Fe_6O_8Ru_4S_7$
Formula weight	294.19	713.56	1606.39	1962.95
Colour, habit	Orange, irregular	Yellow–orange, prism	Orange, prism	Red–orange, plate
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1/n$	$C2/c$
a (Å)	9.014(2)	13.733(4)	16.942(2)	12.524(2)
b (Å)	20.032(2)	19.886(2)	17.874(2)	24.202(3)
c (Å)	7.313(2)	8.140(3)	19.538(3)	22.991(3)
β (°)	90	90	105.77(1)	95.32(2)
V (Å^3)	1320.4(4)	2223(1)	5693(1)	6938(1)
Z	4	4	4	4
ρ_{calc} (g cm^{-3})	1.480	2.132	1.874	1.879
F(000)	608	1368	3160	3880
μ(Mo-K_α) (cm^{-1})	12.76	21.08	22.39	23.22
Crystal size (mm)	0.20 × 0.25 × 0.30	0.25 × 0.25 × 0.35	0.10 × 0.18 × 0.30	0.03 × 0.20 × 0.22
Transmission factors	0.89–1.00	0.94–1.00	0.77–1.00	0.81–1.00
Scan type	ω–2θ	ω–2θ	ω–2θ	ω–2θ
Scan range ω (°)	$1.31+0.35 \tan\theta$	$1.21+0.35 \tan\theta$	$1.00+0.35 \tan\theta$	$1.00+0.35 \tan\theta$
Scan rate (° min^{-1})	16 (8 rescans)	32 (8 rescans)	16 (8 rescans)	8 (8 rescans)
Data collected	$+h, +k, +l$	$+h, +k, +l$	$+h, +k, +l$	$+h, +k, +l$
$2\theta_{max}$ (°)	65	70	55	55
Crystal/decay/(%)	negligible	negligible	negligible	negligible
Total reflections	2756	5456	13 939	8534
Unique reflections	2756	5456	13 492	8159
R_{merge}	—	—	0.050	0.047
Number with $I \geqslant 3\sigma(I)$	1499	3144	5154	3382
Variables	164	290	685	420
R	0.029	0.025	0.035	0.035
R_w	0.027	0.021	0.030	0.033
Gof	1.64	1.31	1.30	1.33
Max. Δ/σ (final cycle)	0.06	0.03	0.02	0.02
Residual density (e Å^{-3})	−0.22 to 0.25	−0.61 to 0.72 (near Ru)	−0.47 to 0.46 (near Ru)	−0.78 to 0.77 (near Ru)

[a] Temperature 294 K, Rigaku AFC6S diffractometer, Mo-K_α (λ = 0.71069 Å) radiation, graphite monochromator, take-off angle 6.0°, aperture 6.0 × 6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan/background time ratio 2 : 1), $\sigma^2(F^2) = [S^2(C+4B)]/Lp^2$ (S = scan rate, C = scan count, B = normalized background count), function minimized $\Sigma w(|F_o|-|F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$, $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $R_w = (\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2)^{1/2}$, and gof $= [\Sigma w(|F_o|-|F_c|)^2/(m-n)]^{1/2}$. Values given for R, R_w and gof are based on those reflections with $I \geqslant 3\sigma(I)$.

was initiated in the centrosymmetric space group $C2/c$ on the basis of the E-statistics and Patterson function. This choice was confirmed by subsequent calculations. Complex **10** has exact (crystallographic) C_2 symmetry, the axis passing through the central μ_4-sulphur atom.

All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were fixed in calculated positions (C—H = 0.99 Å for **6**, **9** and **10**; and 0.98 Å for **7**, $B_H = 1.2 B_{\text{bonded atom}}$). Secondary extinction corrections (Zachariasen Type) were applied for **6** and **7**, the final values of the extinction coefficients being $7.1(1) \times 10^{-6}$ and $5.9(1) \times 10^{-6}$, respectively. The chlorine atoms of one of the two chloroform solvate molecules in **9** were disordered with respect to rotation about the C—H bond. A split-atom model was employed, the population parameters being adjusted as the refinement progressed to give approximately equal average thermal parameters for the two components of the disorder. Neutral atom scattering factors for all atoms[9a] and anomalous dispersion corrections for the non-hydrogen atoms[9b] were taken from the *International Tables for X-ray Crystallography*. Parallel refinements of the mirror-image structures of **6** and **7** gave significantly higher residuals. Selected bond lengths and angles are listed in Tables 2 and 3. Final atomic coordinates and equivalent isotropic thermal parameters, bond lengths and bond angles, hydrogen atom parameters, anisotropic thermal parameters, bond lengths, bond angles, torsion angles, intermolecular contacts, and least-squares planes for all four structures are available as supplementary material.

RESULTS AND DISCUSSION

The reaction of $Ru_3(CO)_{12}$ *with* SPh_2

The reaction of $Ru_3(CO)_{12}$ with SPh_2 in toluene for 15 h affords three products as judged by TLC, none of which contain any hydrides as revealed by ^1H NMR spectroscopy.

Complex **7** was isolated as the only major product from the reaction in 70% yield. The ^1H NMR spectrum shows the presence of two phenyl groups, one of which is shifted upfield appreciably. The mass spectrum gives a parent ion at m/z 715 corresponding to a formula such as $Ru_3(CO)_8(SPh_2)$. Its structure was established by using X-ray crystallography and an ORTEP diagram of the molecule is shown in Fig. 1.

The structure of **7** consists of an open Ru_3 triangle with the open edge bridged by an η^1 and η^6 bonded aryl, C_6H_5, moiety. The Ru(1)—Ru(2)—Ru(3) angle is 86.80(2)° and the Ru(1)Ru(2)Ru(3)C(1) torsion angle is very small at 4.8(1)°. The Ru(2)—Ru(3) edge is bridged by a thiolate SPh moiety. Ru(1) is bonded to two carbonyls, Ru(2) and Ru(3) are each bonded to three carbonyls; thus, the whole cluster is electron precise. The Ru(1)

Table 2. Selected bond lengths (Å)[a] for **6**, **7**, **9** and **10** with estimated standard deviations in parentheses

6	Fe(1)—Cp(1)	1.63	**9**	Ru(1)—Ru(2)	2.8560(9)
	S(1)—C(1)	1.752(4)		Ru(1)—S(1)	2.408(2)
	Fe(1)—Cp(2)	1.65		Ru(1)—S(3)	2.373(2)
	S(1)—C(11)	1.766(3)		Ru(2)—S(1)	2.415(2)
				Ru(2)—S(4)	2.368(2)
7	Ru(1)—Ru(2)	2.9093(6)		Ru(3)—S(4)	2.421(2)
	Ru(1)—C(1)	2.308(5)		Ru(1)—Ru(3)	3.0723(9)
	Ru(1)—C(2)	2.266(5)		Ru(1)—S(2)	2.369(2)
	Ru(1)—C(3)	2.281(5)		Ru(2)—Ru(3)	3.1320(9)
	Ru(1)—C(4)	2.306(5)		Ru(2)—S(2)	2.379(2)
	Ru(1)—C(5)	2.286(5)		Ru(3)—S(3)	2.424(2)
	Ru(1)—C(6)	2.271(5)			
	Ru(2)—Ru(3)	2.7691(8)	**10**	Ru(1)—S(1)	2.562(1)
	Ru(2)—S(1)	2.392(1)		Ru(1)—S(3)	2.424(2)
	Ru(3)—S(1)	2.394(1)		Ru(2)—S(1)	2.588(1)
	Ru(3)—C(1)	2.119(4)		Ru(2)—S(3)	2.442(2)
	S(1)—C(7)	1.796(4)		Ru(1)—S(2)	2.399(2)
				Ru(1)—S(4)	2.397(2)
				Ru(2)—S(2)	2.408(2)

[a] Cp(1) and Cp(2) refer to the unweighted centriods of the C(1)–C(5) and C(6)–C(10) cyclopentadienyl rings, respectively.

Table 3. Selected bond angles (°) for **6**, **7**, **9** and **10** with estimated standard deviations in parentheses

6	Cp(1)—Fe(1)—Cp(2)	177.3
	C(1)—S(1)—C(11)	103.1(2)
7	Ru(1)—Ru(2)—Ru(3)	86.80(2)
	Ru(1)—Ru(2)—S(1)	85.67(3)
	Ru(3)—Ru(2)—S(1)	54.69(3)
	Ru(2)—Ru(3)—S(1)	54.61(3)
	Ru(2)—S(1)—Ru(3)	70.70(3)
9	Ru(2)—Ru(1)—Ru(3)	63.66(2)
	Ru(2)—Ru(1)—S(2)	53.19(4)
	Ru(3)—Ru(1)—S(1)	89.08(5)
	Ru(3)—Ru(1)—S(3)	50.92(5)
	S(1)—Ru(1)—S(3)	81.23(6)
	Ru(1)—Ru(2)—S(1)	53.57(4)
	S(1)—Ru(2)—S(2)	80.05(6)
	Ru(1)—Ru(3)—Ru(2)	54.81(2)
	Ru(2)—Ru(1)—S(1)	53.80(5)
	Ru(1)—Ru(2)—Ru(3)	61.53(2)
	Ru(1)—Ru(2)—S(2)	52.85(4)
	Ru(1)—Ru(3)—S(3)	49.44(4)
	Ru(1)—S(2)—Ru(2)	73.96(5)
	Ru(2)—S(4)—Ru(3)	81.66(6)
	Ru(2)—Ru(3)—S(4)	48.44(4)
	S(3)—Ru(3)—S(4)	92.44(6)
	Ru(1)—S(1)—Ru(2)	72.62(5)
	Ru(1)—S(3)—Ru(3)	79.64(6)
10	S(1)—Ru(1)—S(2)	85.96(5)
	S(1)—Ru(1)—S(4)	88.26(5)
	S(2)—Ru(1)—S(4)	166.28(7)
	S(1)—Ru(2)—S(3)	82.89(6)
	S(2)—Ru(2)—S(3)	80.86(6)
	Ru(1)—S(1)—Ru(2)	75.75(4)
	Ru(1)—S(3)—Ru(2)	81.06(5)
	S(1)—Ru(1)—S(3)	83.78(6)
	S(2)—Ru(1)—S(3)	81.39(7)
	S(3)—Ru(1)—S(4)	85.62(7)
	S(1)—Ru(2)—S(2)	85.21(5)

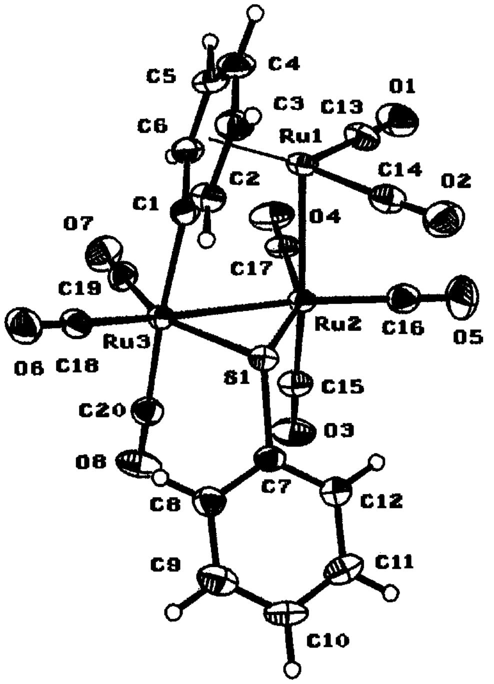


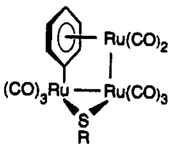
Fig. 1. ORTEP diagram of **7**; 33% probability ellipsoids are shown.

centre has a typical three-leg piano stool geometry, and the other two ruthenium centres have approximate octahedral geometry.

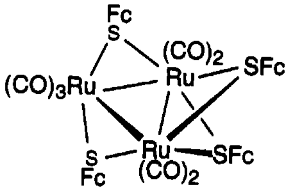
The C_6H_5 group on sulphur is *anti* to the σ, π-bonded C_6H_5 moiety, as would be expected for such a structure. The thiolate bridged Ru(2)—Ru(3) bond at 2.7691(8) Å is much shorter than the unbridged Ru(1)—Ru(2) bond at 2.9093(6) Å, and the thiolate bridge is symmetrical [2.392(1) and 2.394(1) Å, respectively]. The aryl C(1)—C(6) ring is bonded to Ru(3) via a σ bond of length 2.119(4) Å and η^6 bonded to Ru(1). The Ru(1)—C [C(1)–C(6) ring] distances range from 2.266(5) to 2.308(5) Å, with an average of 2.286 Å.

There is noticeable C—C bond lengthening in the C(1)–C(6) ring; the C(1)—C(2), C(1)—C(6) and C(2)—C(3) bonds (av. 1.428 Å) are longer than the other three (av. 1.395 Å), and these should be compared with the C—C bonds in the C(7)–C(12) ring (av. 1.379 Å). While all C—C—C angles in the C(7)–C(12) ring are close to 120°, the C(2)—C(1)—C(6) angle of 113.3(4)° is significantly smaller than the rest, which range from 117.6(4) to 123.7(4)°.

As described in the Introduction, orthometallation of phenyl groups is a well known and facile process for arylphosphines and many of their reactions with metal carbonyl clusters seem to proceed through this step. On this basis orthometallation is also expected to be facile for aryl sulphides, yet the structure of **7** shows that orthometallation is not a major pathway in the reaction of Ph_2S with $Ru_3(CO)_{12}$. A phenyl C—S bond is cleaved while all the C—H bonds remain intact. Only a few other cleavage reactions of this type are known: for example, compounds **11** and **12** can be obtained by reacting $Ru_3(CO)_{12}$ with P(2-Py)PhR (R = Ph or 2-Py).[10,11] An older example is **13**, isolated as one of the nine products of the reaction of $Os_3(CO)_{12}$ with PPh_3.[12,13] It is suggested that **11** and **12** are formed by migration of aryl moieties, resulting in a phosphido group that bridges two non-bonded ruthenium atoms. The analogous sulphide groups in **7** bridges two bonded ruthenium atoms so that processes involving oxidative addition of S—Ph to an $Ru(CO)_4$ moiety cannot be ruled out in this case.



7 **R = Ph**
8 **R = Fc**



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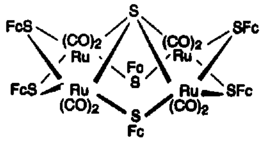

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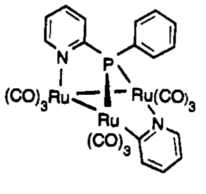

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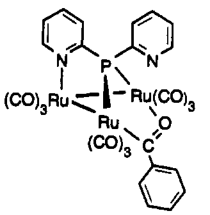

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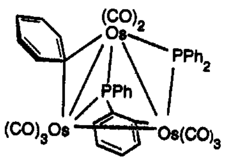

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The reaction of $Ru_3(CO)_{12}$ *with* SFcPh

In order to investigate the relative reactivity of SPh and SFc moieties, $Ru_3(CO)_{12}$ was heated with the mixed sulphide SFcPh. This reaction proceeds in refluxing toluene (11 h) and affords one major product **8** and some minor ones, of which **9** and **10** were isolated in sufficient amounts for X-ray structure determinations following painstaking chromatographic clean up.

The ^{1}H NMR spectrum of **8** is very similar to that of **7** in the phenyl region and shows normal ferrocenyl resonances. The mass spectrum shows a parent ion at m/z 823 corresponding to the formula $Ru_3(CO)_8(SFc)Ph$. Thus, the structure of **8** is undoubtedly analogous to that of **7**.

Our work with phosphines containing both Ph and Fc groups reveals that P—Ph is metallated in preference to P—Fc, resulting in benzyne rather than ferrocyne cluster complexes. Clearly, in the $Ru_3(CO)_{12}$/sulphide systems metallation is not facile, hydrides are not formed and S—Ph cleavage dominates. The structures of the minor products **9** and **10** (Figs 2 and 3) emphasize this point further. Apart from the central sulphur atoms of **10**, all the sulphur atoms have lost phenyl groups and have retained ferrocenyl moieties.

The structure of **9** consists of an Ru_3 triangle with one short Ru(1)—Ru(2) bond [2.8560(9) Å] symmetrically bridged by two SFc groups;

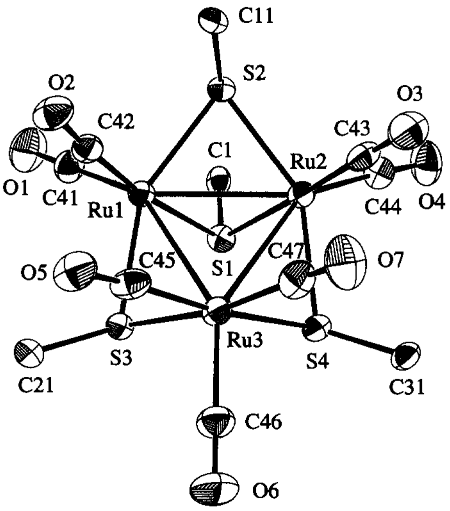

Fig. 2. ORTEP diagram of **9**; 33% probability ellipsoids are shown. Fc groups are omitted for clarity.

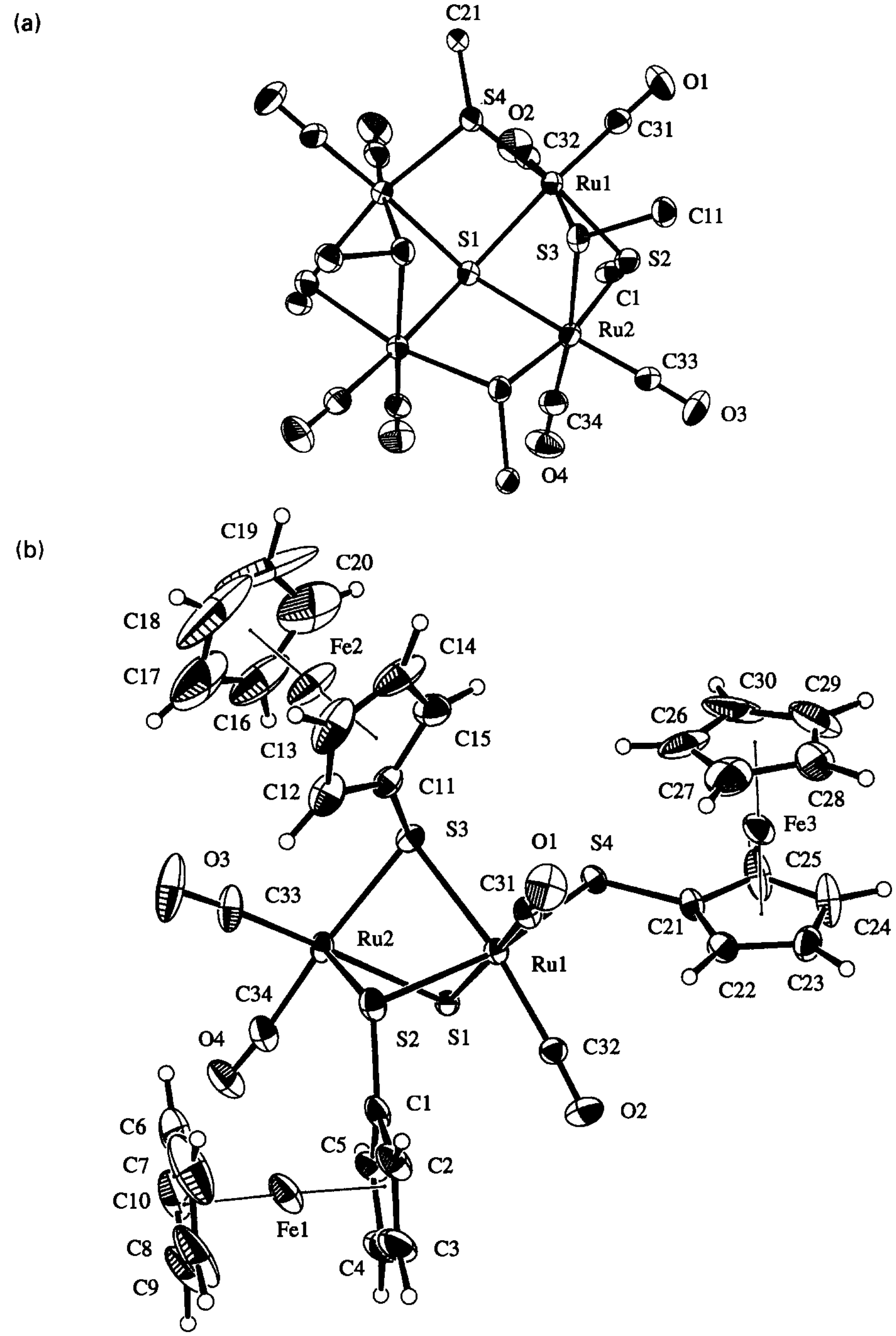

Fig. 3. ORTEP diagrams of **10**; 33% probability ellipsoids are shown. (a) Full diagram but Fc groups have been omitted for clarity. (b) Partial diagram showing orientation of Fc groups.

however, the Ru—S bond lengths in the bridge are not equal [Ru(1)—S(2) = 2.369(2) Å; Ru(2)—S(2) = 2.379(2) Å; Ru(1)—S(1) = 2.408(2) Å; Ru(2)—S(1) = 2.415(2) Å]. The longer bonds are *trans* to CO groups. There are two long Ru(1)—Ru(3) and Ru(2)—Ru(3) bonds [3.0723(9) and 3.1320(9) Å, respectively] unsymmetrically bridged by SFc groups [e.g. Ru(2)—S(4) = 2.368(2) and Ru(3)—S(4) = 2.421(2) Å]. The molecule also has two terminal CO groups on both Ru(1) and Ru(2) and three on Ru(3). The Ru—CO bond lengths at Ru(1) and Ru(2) are shorter on average (1.881 Å) than those of Ru(3) (1.991 Å).

An alternative way of looking at **9** is as an almost planar Ru(1)Ru(2)S(4)S(3) fragment [torsion angle = $-0.91(7)^\circ$, $\chi^2 = 194$] capped by the

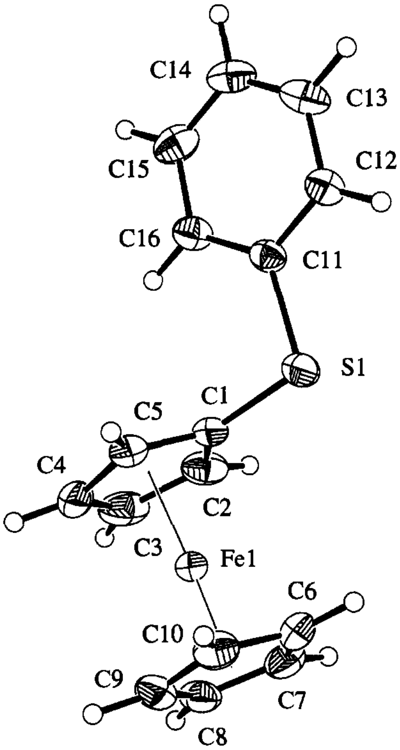

Fig. 4. ORTEP diagram of **6**; 33% probability ellipsoids are shown.

Ru(3)(CO)$_3$ moiety. S(2) is only 0.02 Å from the Ru$_2$S$_2$ plane. However, these structural features have no precedent in the Cambridge Data Base.[14]

The electron count of 50 suggests that there should be only two Ru—Ru bonds and these would have to be the long, greater than 3 Å, Ru(2)—Ru(3) and Ru(1)—Ru(2) interactions, leaving the short Ru(1)—Ru(2) interaction of 2.8560(9) Å to be maintained only by the two bridging SFc moieties.

Some theory[15–18] applied to other 50-electron phosphido-bridged species such as Ru$_3$(CO)$_7$(μ-Cl)(μ-PPh$_2$)$_3$ and Os$_3$(CO)$_7$(μ_2:η^2-C$\equiv$CPh)$_2$(μ-PPh$_2$)$_2$,[15] which have the 'two long, one short M—M bond' pattern, and Ru$_3$(CO)$_9$(μ_3-PPh(C$_6$H$_4$N)(μ-PPh$_2$),[20] which has two bonding Ru—Ru interactions [2.916(1) and 2.870(1) Å] and one non-bonding at 3.847(1) Å, suggesting that the HOMO of these molecules is a three-centre metal–metal bonding MO. However, the other bonding MOs, involving the bridging groups, are anti-bonding with respect to the metal–metal bonds, resulting in cluster core expansion. Presumably, the bonding in **9** can be described in similar terms.

The molecular structure **10** has C_2 symmetry and consists of four ruthenium atoms μ-bridged by a central (but not co-planar) sulphur atom S(1): Ru(1)—S(1) at 2.562(1) Å is a similar length to Ru(2)—S(1) at 2.588(1) Å. There are no Ru—Ru bonds and each ruthenium bears two terminal CO groups.

Two of the Ru–Ru vectors are bridged by single symmetrical SFc bridges [Ru(1)—S(4) = Ru(4)—S(4) = 2.397(2) Å] and the other two are each bridged symmetrically by two S—Fc moieties [e.g. Ru(1)—S(2) = 2.399(2) and Ru(2)—S(2) = 2.408(2) Å; Ru(2)—S(3) = 2.442(2) and Ru(1)—S(3) = 2.424(2) Å], although the bonds on the 'S(1) side' of the molecule, i.e. to S(2), are shorter. This is not unexpected because S(2) is *trans* to two SFc moieties and S(3) is *trans* to two CO groups. This bond length difference, also noted in **9**, is reflected in the Ru—CO distances: e.g. Ru(2)—C(34)O at 1.911(9) Å, which is *trans* to S(3)—Fc, is longer than Ru(2)—C(33)O at 1.845(9) Å, which is *trans* to S(1).

The electron count for **10** is 70, two less than the electron precise 72, if S(1) contributes four electrons. There are no ruthenium analogues of this structure in the Cambridge Data Base,[14] although the central core of (Et$_4$N)$_4$Fe$_6$S$_9$(SBz)$_2\cdot$H$_2$O and related molecules shows some similarity to **10**.[15–17, 21–23] The bonding network in the related 64-electron complex Ni$_4$(μ-SC$_6$H$_{11}$)$_8$ (no Ni—Ni bonds) has been discussed by Mealli and Proserpio.[18]

During the course of our SFcPh studies we inadvertently redetermined the structure of this compound. The first determination was made by Adeleke *et al.*:[24] the orthorhombic space group was $P2_12_12_1$ and the R value was 0.026. Our redetermination found the same space group and the R value was 0.029. The new structure, which used data out to $2\theta = 65.0°$, is slightly more accurate, although the main features are the same as noted previously, Fig. 4. The C$_6$-phenyl plane is almost perpendicular to, and over the centre of, the C$_5$-cyclopentadienyl plane: dihedral angle = 86.24° and the torsion angle C(1)S(1)C(11)C(16) = 6.5(3)°. The Ph—S—Fc angle is 103.1(2)°.

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