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HYDROCARBON METAL SULPHIDE COMPLEXES

VI*. A NEW TYPE OF REARRANGEMENT OF A CYCLOPENTADIENYL-RUTHENIUM COMPLEX

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Summary

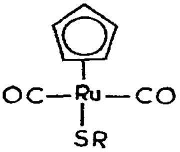
The complexes $C_5H_5Ru(CO)_2SR$ (R = C_6F_5 or CH_3) undergo photochemical conversion to binuclear and trinuclear derivatives which exhibit isomerism. A novel rearrangement has been detected for $[C_5H_5Ru(CO)(SC_6F_5)]_2$.

Discussion

Similar derivatives of each metal of a triad frequently exhibit wide differences in behaviour, the tendency towards polynuclear complex formation being more pronounced with second and third row metals. Since the chemistry of cyclopentadienyliron sulphide complexes had been so extensively investigated [1—10] a comparative study of analogous ruthenium complexes seemed worthwhile, in anticipation of discovering alternative bonding arrangements. It had already been observed in the cyclopentadienyliron dicarbonyl series that CH_3S [2] and C_6F_5S [1, 10] derivatives represented opposite extremes of reactivity, so only these ruthenium analogues were studied.

A. Pentafluorophenylthio complexes of ruthenium

The terminal pentafluorophenylthio complex (I, R = C_6F_5) was prepared



(I)

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* This paper is abstracted in part from the Ph.D. thesis submitted by A.P. to University of Strathclyde, September 1970. For part V of the series, see ref. 1.

TABLE 1

PHYSICAL PROPERTIES OF THE COMPLEXES $CpM(CO)_2SR$ (M = Ru, Fe [a]; R = C_6F_5, CH_3)

Compound	M.p. (°C)	IR (cm^{-1}) ν(CO)	^1H NMR (τ)		^{19}F NMR [b]		
			Cp	CH_3	o-F	m-F	p-F
$CpRu(CO)_2SC_6F_5$	90—92	2047vs [c] 2000vs	4.48 [c]		132.8 [c]	163.5 [c]	154.1 [c]
$CpFe(CO)_2SC_6F_5$	95—96	2042 [c] 1990	5.05 [d]		131.3 [e]	164.3 [e]	160.2 [e]
$CpRu(CO)_2SCH_3$	60	2040vs [c] 1985vs	4.58 [c]	8.12 [c]			
$CpFe(CO)_2SCH_3$	72	2029 [c] 1981	5.13 [c]	8.42 [c]			

[a] Ref. 1, 2, 23. [b] Chemical shifts (ppm) upfield from internal $CFCl_3$ (0.0 ppm). [c] In CCl_4. [d] In CS_2. [e] In acetone.

in good yield from the corresponding chloride $CpRu(CO)_2Cl$ [11] using a method developed previously for analogous complexes of tungsten, molybdenum [12], chromium [13], iron [2] and manganese. The physical properties of this material are collected in Table 1. Like the iron analogue this material did not decompose in refluxing benzene but by contrast the ruthenium complex did 'dimerise' * photochemically under conditions where the iron complex was unaffected. The course of the photochemical reaction over 24 h was monitored most conveniently by multisampling TLC techniques which showed that the starting material had decomposed completely after ≈ 5 h and three new compounds had been formed. An orange compound II had maximum concentration after 1—2 h irradiation and had completely disappeared after 24 h. A red compound III had maximum concentration at 0.5 h irradiation but decreased in concentration progressively thereafter. A third, deep red, compound IV was present in small amounts after 0.5 h irradiation and was present in its greatest amount after 24 h. To obtain sufficient quantities of each of these materials for characterisation purposes a number of preparative irradiation experiments was conducted for the appropriate times and the products separated by column chromatography. The physical properties of these compounds are collated in Table 2.

The solid orange compound II was isolated pure only with considerable difficulty because it was very labile in solution. A mass spectrum indicated a molecular formula $[C_5H_5Ru(CO)SC_6F_5]_2$ and produced a cracking pattern similar to related iron complexes. The IR spectrum of a freshly prepared solution of II showed only terminal metal carbonyl absorptions at 1980s and 1958m cm^{-1}, which may be compared with the values [2] of the separable 'stable' and 'unstable' isomers of $[CpFe(CO)SPh]_2$ at 1978 and 1938 cm^{-1} respectively. An ^1H NMR spectrum of II showed two C_5H_5 signals at τ 5.30 and τ 5.39 in the intensity ratio of 2/1 respectively. It therefore seems that II was obtained as a 2/1 mixture of isomers and although on this basis alone the assignment of stereochemistry is uncertain, it is tentatively suggested that the predominant derivative V exhibiting ν(CO) at 1980 cm^{-1} and a chemical shift of τ 5.30 corresponds to the iron complex of known structure [4].

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* The term 'dimerise' is used loosely in this paper to describe the process by which a binuclear complex is produced from I, even though elimination of ligands occurs.

SCHEME 1

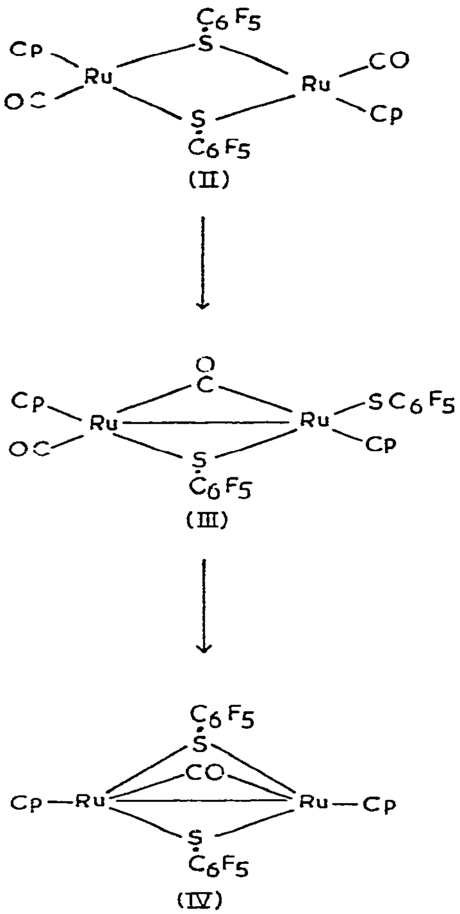
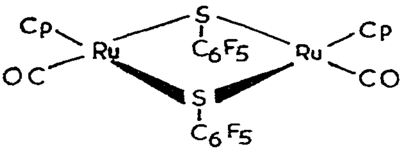


TABLE 2

PHYSICAL PROPERTIES OF COMPOUNDS II, III AND IV

Compound	M.p. (°C)	Mol. wt. [a]	IR (cm^{-1}) [b] ν(CO)	^{1}H NMR (τ) [b] Cp	^{19}F NMR [b,c] o-F	m-F	p-F
II	153 [d]	787.8	1980s 1958m	5.30(2) 5.39(1)			
III	221	787.8 790 [e]	1945s 1805m	5.10 [f]			
IV	206	759.8	1795s	5.03	132.9 (2F) 136.2 (2F)	165.5 (2F) 166.5 (2F)	159.7 (2F)

[a] By mass spectrometry unless otherwise stated. [b] Solution spectra in CCl_4. [c] Chemical shifts (ppm) upfield from internal $CFCl_3$ (0.0 ppm). [d] Isomerises to III at 153°, melts ≈ 221°. [e] Osmometrically in chloroform. [f] Two singlets, separation 1 Hz.



(V)

The red compound III was isomeric with II according to mass spectroscopic information, but the cracking pattern was quite different. Whereas the molecular ion of II lost two carbonyl groups stepwise according to established behaviour [14], only a single carbonyl group was lost from III before cleavage of an SC_6F_5 group Infrared spectra of III in solution showed both terminal [ν(CO) 1945s cm^{-1}] and bridging [ν(CO) 1805m cm^{-1}] carbonyl groups whilst ^1H NMR spectra indicated two cyclopentadienyl groups in different environments, but no evidence for Ru—H bonds. Furthermore there was no change in the appearance of these ^1H NMR spectra between —40° and +62° but low solubility prevented measurement of ^{19}F NMR spectra. These data are accommodated by structure III but without additional information the stereochemistry cannot be determined.

The remaining product IV, a deep-red crystalline compound was shown by mass spectrometry to have the molecular formula $[\{C_5H_5Ru(SC_6F_5)\}_2CO]$ corresponding to loss of one CO molecule from II and/or III. The IR spectrum showed only a single peak in the metal carbonyl region at 1795 cm^{-1}, indicating a bridging carbonyl group, whilst an ^1H NMR spectrum was characterised by a sharp singlet at τ 5.03 with no resonance signals above τ 10. ^{19}F NMR spectra of this complex (Table 2) showed two distinct 'types' of C_6F_5-rings, although there was accidental coincidence of chemical shift of the *p*-fluoro atoms of each. All these spectroscopic features can be accommodated by postulating the gross structure IV with one bridging CO group, two bridging C_6F_5S groups and a metal—metal bond to account for the observed diamagnetism of this new class of complex. The non-equivalence of the C_6F_5 groups may reflect the two different orientations possible about each sulphur atom.

B. Transformations of complexes II, III and IV

Reference has been made to the instability of compound II. Thus on heating a pure sample of this material in a sealed, evacuated capillary the orange powder changed sharply to a red solid at 153°. On continued heating this solid melted around 221°, the m.p. of III. Also, this newly-formed red solid had an R_f value identical to that of III. When a pure sample (by IR) of II was run on a TLC plate, two spots were observed, one corresponding to unchanged II and the other to III. Therefore the instability of II is due to its facile isomerisation to III. Pure samples of III, on heating in solution or on UV irradiation for up to 24 h yielded mixtures of III and IV indicating the transformation III → IV but there was no evidence for the conversion of III → II. Compound IV was slowly decomposed on prolonged irradiation but was thermally stable. The transformations described above and shown in Scheme 1, together with the sequential analyses of the reaction mixture, suggest that II and III may be produced independently from (I, R = C_6F_5) but that II is the major source of III. The decarbonylation reaction involved in forming IV resembles a simple S_N2 reaction in which the attacking nucleophile is held in position by the stereochemical constraints of the molecule.

TABLE 3

SPECTROSCOPIC PROPERTIES OF THE COMPLEXES $[CpM(CO)SCH_3]_2$, (M = Ru, Fe [a])

Compound	Isomer	IR (cm^{-1}) ν(CO)	^1H NMR (τ)	
			Cp	CH_3
$[CpRu(CO)SCH_3]_2$	Isomer (*i*)	1958s [b]	5.18 [b]	8.00
$[CpRu(CO)SCH_3]_2$	Isomer (*ii*)	1935m [b]	5.15 [b]	7.86
$[CpFe(CO)SCH_3]_2$	'Stable'	1951 [b]	5.74 [c]	8.69
$[CpFe(CO)SCH_3]_2$	'Unstable'	1929 [b]	5.78 [c]	8.42

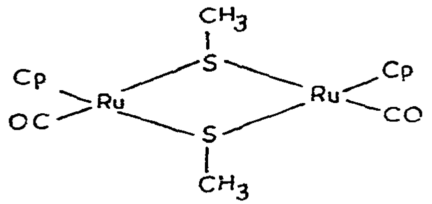
[a] Ref. 2. [b] In CCl_4. [c] In CS_2.

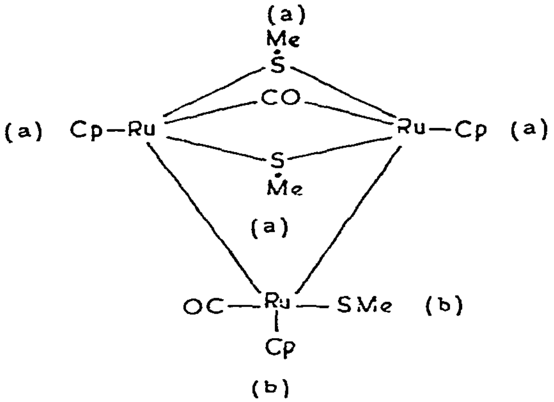
The type of irreversible isomerisation II → III, which involves two different types of bridging and terminal ligand, is unique in organometallic chemistry. Since it involves only a redistribution of bonds in the molecule, it falls within the definition of a desmotropic rearrangement (Greek: change of bonds) [15, 16]. There is implied therefore, a difference between this rearrangement and those reversible processes occurring between bridged and non-bridged forms of, for example, $[CpFe(CO)_2]_2$ [17—22] and $[CpFe(CO)_2 \cdot Co(CO)_4]$ [20], which ultimately lead to carbonyl scrambling. It is noteworthy that whereas ruthenium analogues of the latter compounds prefer non-bridged forms, by contrast the compounds described here show a tendency towards multiple bridging.

C. Methylthio complexes of ruthenium

The terminal methylthio complex I(R = CH_3) was obtained as an orange air-stable crystalline solid from $CpRu(CO)_2Cl$, by reaction with $Et_3NH^{+-}SCH_3$ in refluxing benzene. (See Table 1 for properties of I). Under thermal conditions (refluxing in toluene for 17 h), complex I(R = CH_3) afforded the di-μ-methylthio complex VI, as a pair of isomers. Thus, the elemental analyses corresponded to a molecular formulation of $[CpRu(CO)SCH_3]_2$, and two orange spots moving close together were observed on a TLC plate. In the IR spectrum, there were terminal metal carbonyl absorptions only, at 1958s and 1935m cm^{-1}. The ^1H NMR spectrum showed a Cp singlet at τ 5.18 and a CH_3 singlet at τ 8.00, the ratio of the integrals being 5/3. There was also a Cp singlet at τ 5.15 and a CH_3 singlet at τ 7.86, the ratio again being 5/3. The ratio of intensities of Cp (τ 5.18)/Cp(τ 5.15) was equal to the intensity ratio CH_3 (τ 8.00)/CH_3 (τ 7.86), the value being approximately 1.0/0.4. This suggests that the terminal mercaptide I(R = CH_3) dimerises to a pair of isomers of VI, the ratio of the isomer concentrations in solution being 0.4/1. Thus, assuming that the stronger carbonyl frequency (1958 cm^{-1}) belongs to the isomer which gives rise to the stronger ^1H NMR signals, then the spectroscopic properties of the two isomers can be assigned as in Table 3. The values for the isomers of VI correspond closely to those obtained for the stable and unstable isomers of the analogous iron complex $[CpFe(CO)SCH_3]_2$ [2] (Table 3). Again a definite assignment of both isomeric structures is not possible at present but it is likely that the compound having ν(CO) 1958 cm^{-1} has a structure [4, 5] corresponding to V.

Irradiation of $CpRu(CO)_2SCH_3$ for 1.75 h resulted in complete photolysis of starting material, and gave rise to traces of the two isomers of VI already obtained thermally (shown by IR and TLC), as well as a new product VII. This product was obtained as a red crystalline solid whose mass spectrum indicated a molecular formula corresponding to $[(CpRuSCH_3)_3(CO)_2]$, and whose IR spectrum indicated both terminal and bridging carbonyl groups at 1940s and 1770m cm^{-1}, respectively. The ^1H NMR spectrum showed two Cp resonance signals at τ 5.07 and τ 5.27, and two CH_3 signals at τ 7.34 and τ 7.78, the intensity ratio of the total Cp/CH_3 signals being 5/3. The intensity ratio Cp(τ 5.07)/Cp(τ 5.27) was equal to the ratio CH_3 (τ 7.78)/CH_3 (τ 7.34), the value being 2/1. There were no Ru—H signals above τ 10. Thus, the ^1H NMR spectrum suggested the presence of one distinct and two equivalent Cp rings in the complex as well as one distinct and two equivalent CH_3 groups. These features are accommodated by the postulated structure VII in which the two types of groups are labelled (a) and (b).


(VI)



(VII)

In summary, the terminal mercaptide complexes of ruthenium (I, R = CH_3 and C_6F_5) were more reactive under photolytic conditions than their iron analogues. Thus whereas $CpFe(CO)_2SC_6F_5$ was stable to irradiation conditions, $CpRu(CO)_2SC_6F_5$ gave, on UV irradiation, three binuclear complexes. In addition, the close similarity in character of the CO and SC_6F_5 groups as bridging ligands in these ruthenium complexes allowed a novel type of isomerisation to be observed. Also, $CpRu(CO)_2SCH_3$ gave a binuclear complex on heating, and a trinuclear complex on irradiation, while $CpFe(CO)_2SCH_3$ gave only binuclear species on heating or on irradiation.

Experimental

For general procedures see Part 1 [2].

Preparation of (pentafluorophenylthio)cyclopentadienyldicarbonylruthenium (I, R = C_6F_5)

To a solution of chlorocyclopentadienyldicarbonylruthenium (1.0 g, 3.9 mmole) in benzene (50 ml) was added excess pentafluorothiophenol (10.0 g, 50 mmole) and triethylamine (1.0 g, 10 mmole). The solution was heated at 50° for 18 h then cooled to room temperature and the benzene evaporated. The excess pentafluorothiophenol was removed under vacuum (0.1 mm/35°), to give a brown gummy residue. This was dissolved in ether and chromatographed on Florisil. Elution with petrol/ether (99/1) removed most of the white solid di(pentafluorphenyl) disulphide formed during the reaction, and petrol/ether (95/5) gave (pentafluorophenylthio)cyclopentadienyldicarbonylruthenium as a yellow solid (1.2 g, 74%) m.p. 90—92°, slightly contaminated with the disulphide. Repeated, careful chromatography or recrystallisation did not remove completely the impurity (found: C, 39.73; H, 1.77; S, 9.23; P^+, *m/e* 421.8952. $C_{13}H_5F_5O_2{}^{102}RuS$ calcd.: C, 37.02; H, 1.19; S, 7.60%; P^+, *m/e* 421.8967).

Attempted thermal dimerisation of (pentafluorophenylthio)cyclopentadienyldicarbonylruthenium

In an attempt to dimerise (pentafluorophenylthio)cyclopentadienyldicarbonylruthenium under thermal conditions, the compound (50 mg) was refluxed for 24 h in benzene. The IR spectrum of the product after this time was superimposable on that of the starting material, showing that the compound did not react in any way on heating.

Trial irradiation of (pentafluorophenylthio)cyclopentadienyldicarbonylruthenium (I)

(Pentafluorophenylthio)cyclopentadienyldicarbonylruthenium (220 mg) in benzene (400 ml) was irradiated with UV light. 5 ml portions of the solution were withdrawn at intervals over a period of 24 h, the volume reduced to small bulk, and the concentrated sample stored at low temperature in the dark to prevent any further reaction. The samples were then run together on a wide silica TLC plate (20 X 20 cm) and the following points were noted:

1. The starting material had apparently disappeared completely after 5 h irradiation. (The pale yellow spot could hardly be detected after 0.5 h).

2. Three new compounds (II—IV) were formed during the course of the irradiation.

3. Compound II moved as an orange spot on the TLC plate and had maximum intensity between 1.0—2.0 h irradiation and had completely disappeared after 24 h.

4. Compound III moved as a red spot on the TLC plate and had maximum intensity after 0.5 h. Thereafter its concentration decreased markedly, but not completely, over 24 h.

5. Compound IV moved as a deep red spot on the TLC plate. It was present in small amounts after 0.5 h and its concentration increased steadily over 24 h.

6. Using petrol/ether mixtures, compound IV was eluted first on the TLC plate, followed by (pentafluorophenylthio)cyclopentadienyldicarbonylruthenium, compound II and compound III respectively.

In order to obtain samples of the three compounds, irradiations were carried out for different lengths of time and the products isolated as described (vide infra).

Typical irradiation experiments which describe isolation of II, III and IV

(a). For 12.0 h. (Pentafluorophenylthio)cyclopentadienyldicarbonylruthenium (1.2 g, 2.8 mmole) in benzene (600 ml) was irradiated with UV light for 12 h during which time the original yellow solution had become red in colour. The solution was filtered through kieselguhr, evaporated to small bulk and chromatographed on Florisil. Elution with petrol/ether (98/2) gave a red solution which was evaporated

to an orange-red solid. Recrystallisation from methylene chloride/petrol gave compound II, *di-μ-(pentafluorophenylthio)bis(carbonylcyclopentadienylruthenium* as an orange solid (20 mg, 2%), m.p. 153° (isomerises, see Discussion). IR ($CHCl_3$ 1980s, 1958m cm^{-1}. (Found: P^+, *m/e* 787.80393. $C_{24}H_{10}F_{10}O_2{}^{102}Ru_2S_2$ calcd.: P^+, *m/e* 787.80364.)

Continued elution with petrol/ether (90/10) gave a deep red solid which was recrystallised from methylene chloride/petrol to give compound III, *μ-carbonyl-μ-(pentafluorophenylthio)(carbonylcyclopentadienylruthenium)-[(pentafluorophenylthio)cyclopentadienylruthenium]* as a red solid (217 mg, 20%) m.p. 221°. IR ($CHCl_3$) 1945s, 1805m cm^{-1}. (Found: C, 37.52; H, 2.12; S, 7.89; P^+, *m/e* 788; $P^+ - CO$, *m/e* 760; $P^+ - 2CO$, *m/e* 732. Mol. wt. (osmometric, in chloroform), 790. $C_{24}H_{10}F_{10}O_2{}^{102}Ru_2S_2$ calcd.: C, 36.64; H, 1.28; S, 8.16%. P^+, *m/e* 788; $P^+ - CO$, *m/e* 760; $P^+ - 2CO$, *m/e* 732. Mol. wt. 788).

(b). For 3.5 h. (Pentafluorophenylthio)cyclopentadienyldicarbonylruthenium (1.0 g, 2.4 mmole) in benzene (600 ml) was irradiated with UV light for 3.5 h. The red solution was filtered through kieselguhr, evaporated to small bulk and chromatographed on Florisil. Elution with petrol/ether (95/5) gave a red solution which was evaporated to give a deep red solid. Recrystallisation from methylene chloride/petrol gave IV (8 mg, 1%). In order to characterise the compound, this sample was combined with the material isolated from subsequent preparations. Continued elution with petrol/ether (75/25) gave a red solution which was evaporated to a red solid. Recrystallisation from methylene chloride/petrol gave compound III as a red solid (400 mg, 43%).

(c). For 21.0 h. (Pentafluorophenylthio)cyclopentadienyldicarbonylruthenium (600 mg, 1.4 mmole) in benzene (500 ml) was irradiated with UV light for 21 h. The red solution was filtered through kieselguhr, evaporated to small bulk, and chromatographed on Florisil. Elution with petrol/ether (95/5) gave a red solution which was evaporated to a red solid. Recrystallisation from ether/petrol gave compound IV, *μ-carbonyl-di-μ-(pentafluorophenylthio)bis(cyclopentadienylruthenium)* as a deep red crystalline solid (12 mg, 2%) m.p. 206°. IR ($CHCl_3$) 1795s cm^{-1} (found: P^+, *m/e* 760; $P^+ - CO$, *m/e* 732. $C_{23}H_{10}F_{10}O^{102}Ru_2S_2$ calcd.: P^+, *m/e* 760; $P^+ - CO$, *m/e* 732).

Elution with petrol/ether (50/50) gave a red solution which was evaporated to a red solid. Recrystallization from methylene chloride/petrol gave compound III as a red crystalline solid (120 mg, 21%).

Several irradiation experiments were conducted in THF. For irradiation times less than 5 h the product distribution was similar to that in benzene but after 24 h at least eight uncharacterised products were obtained.

Interconversion of compounds II, III and IV

(a). Effect of heat on compound II. When a sample of compound II was heated in an evacuated capillary tube, the orange colour changed sharply to red at 153°. On continued heating, this newly formed red compound melted sharply at 219°, the approximate melting point of compound III. The melting point tube was broken, and the red compound run on a TLC plate. It was found to have the same R_f value as compound III.

When a sample of compound II was run on a silica TLC plate, two spots were observed. The first orange spot corresponded to unchanged material, and the red spot which followed, corresponded to compound III.

(b). Effect of heat on compound III. A sample of compound III (100 mg) was dissolved in benzene (50 ml) and refluxed for 18 h. The solution was filtered through kieselguhr, reduced to small bulk, and chromatographed on Florisil. Compound IV and compound III were eluted respectively and their identity checked by IR and TLC analyses.

(c). Irradiation of compound III. A sample of compound III (70 mg) was dissolved in benzene (600 ml) and irradiated with UV light for 24 h.

The solution was filtered through kieselguhr and the solvent evaporated to give a red solid. TLC showed this to be a mixture of compound III and compound IV. The pure compounds were obtained by chromatography on a Florisil column and their identity checked by IR and TLC analyses.

(d). Effect of heat on compound IV. Compound IV (15 mg) was dissolved in benzene (50 ml) and refluxed for 18 h. When a sample of the solution was run on a silica TLC plate, only starting material was observed, with no decomposition products.

(e). Irradiation of compound IV. Compound IV (15 mg) was dissolved in benzene (150 ml) and irradiated with UV light for 18 h. After this time some decomposition product was filtered off, and the red filtrate was evaporated to small bulk. TLC showed the presence of starting material only, indicating that compound IV on UV irradiation, undergoes slow decomposition without forming either of compounds II or III.

Preparation of (methylthio)cyclopentadienyldicarbonylruthenium (I,R = CH_3)

To a solution of chlorocyclopentadienyldicarbonylruthenium (600 mg, 2.4 mmole) in benzene (50 ml) were added triethylamine (2.6 ml, 18.0 mmole) and methanethiol (1.0 ml, 18.0 mmole). The mixture was refluxed for 6 h, during which time triethylamine (2.6 ml, 18.0 mmole) and methanethiol (1.0 ml, 18.0 mmole) were again added to compensate for loss of the volatile components. The reaction mixture was filtered through kieselguhr, evaporated to small bulk and chromatographed on Florisil. Elution with petrol/ether (90/10) gave a yellow gum in small yield. This was shown by IR and TLC comparison with an authentic sample to contain a mixture of two isomers of di-μ-(methylthio)bis(carbonylcyclopentadienylruthenium) (VI) (vide infra).

Continued elution with petrol/ether (20/80) gave an orange solid which was recrystallised from ether/petrol to give compound I (R = CH_3) as an orange crystalline solid (237 mg, 38%), m.p. 60° (found: C, 35.38; H, 3.18; S, 11.85. $C_8H_8O_2RuS$ calcd.: C, 35.62; H, 3.00; S, 11.89%).

Preparation of di-μ-(methylthio)bis(carbonylcyclopentadienylruthenium) (VI)

A solution of (methylthio)cyclopentadienyldicarbonylruthenium (300 mg, 1.1 mmole) in toluene (50 ml) was refluxed for 17 h. The solution was filtered through kieselguhr, evaporated to small bulk and chromatographed on Florisil. Elution with petrol/ether (85/15) gave an orange solid which was recrystallised from ether/petrol to give VI as an orange crystalline solid (90 mg, 34%) (found: C, 35.07; H, 3.54; S, 13.05. $C_{14}H_{16}O_2Ru_2S_2$ calcd.: C, 34.84; H, 3.34; S, 13.29%). TLC (silica) showed the presence of two spots moving close together, and both the IR and NMR spectra indicated the presence of two isomers in the sample (see Discussion).

Irradiation of (methylthio)cyclopentadienyldicarbonylruthenium (I, R = CH_3)

Methylthiocyclopentadienyldicarbonylruthenium (225 mg, 0.8 mmole) was dissolved in benzene (300 ml) and irradiated with UV light for 1.75 h, after which time the IR spectrum showed that all the starting material had reacted. The reaction mixture was filtered through kieselguhr, evaporated to small bulk, and chromatographed on Florisil. Elution with petrol gave a mixture of the two isomers of di-μ-(methylthio)bis(carbonylcyclopentadienylruthenium) (VI) as a red powder in low yield (5 mg, 2%). Elution with petrol/ether (70/30) gave a deep red solid, which on recrystallisation from methylene chloride/petrol, gave compound VII (see Discussion) as a red crystalline solid (21 mg, 11%) IR (CCl_4) 1940s and 1770m cm^{-1}. (Found: P^+, m/e 697.8084; P^+-CO, m/e 669.8122. $C_{20}H_{24}O_2{}^{102}Ru_3S_3$ calcd.: P^+, m/e 697.8049; P^+-CO, m/e 669.8100).

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