Organosulphur–Transition-metal Chemistry. Part 4.[1] The Isomerism of μ-Thio- and μ-Seleno-bis[carbonyl(η-cyclopentadienyl)ruthenium] Complexes

By **Stephen D. Killops** and **Selby A. R. Knox,*** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

Complexes $[Ru(CO)_2(ER)(\eta\text{-}C_5H_5)]$ and $[\{Ru(CO)(\mu\text{-}ER)(\eta\text{-}C_5H_5)\}_2]$ are formed when mixtures of $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2]$ and E_2R_2 (ER = SMe, SCH_2Ph, SPh, or SePh) are subjected to u.v. irradiation. With $S_2Bu^t{}_2$, $[Ru(CO)_2(SBu^t)(\eta\text{-}C_5H_5)]$, $[Ru(CO)_2(S_2Bu^t)(\eta\text{-}C_5H_5)]$, and $[Ru_2(CO)_2(\mu\text{-}SBu^t)(\mu\text{-}S_2Bu^t)(\eta\text{-}C_5H_5)_2]$ are produced. On heating or irradiating, $[Ru(CO)_2(ER)(\eta\text{-}C_5H_5)]$ is converted into $[\{Ru(CO)(\mu\text{-}ER)(\eta\text{-}C_5H_5)\}_2]$. The diruthenium complexes, which are concluded to contain a non-planar Ru_2E_2 ring, exist as isomers in which the cyclopentadienyl ligands are *cis* or *trans* with respect to the ring, with additional isomerism arising from the relative orientation of the R groups. Interconversion of *cis* and *trans* isomers occurs on irradiation or heating, relative stabilities depending on the nature of the bridging ER group. Isomers varying only in R-group orientation, however, may be interconverted on the n.m.r. time scale. This is so with *trans*-$[\{Ru(CO)(\mu\text{-}SCH_2Ph)(\eta\text{-}C_5H_5)\}_2]$ and with *cis*- and *trans*-$[\{Ru(CO)(\mu\text{-}SePh)(\eta\text{-}C_5H_5)\}_2]$, each of which exists as a rapidly interconverting mixture of two such isomers, attributed to inversion at sulphur or selenium.

THE existence of two isomers of the thio-bridged complexes $[\{Fe(CO)(\mu\text{-}SR)(\eta\text{-}C_5H_5)\}_2]$ has been established for some years,[2] but their nature has been in doubt. For a planar Fe_2S_2 ring there are five possible isomers, resulting from the varying orientations of the cyclopentadienyl groups and of the lone pair and R group on each sulphur atom. These have been previously designated *cis*-(I)—(III) and *trans*-(I) and -(II). Both *cis*-(II) and *trans*-(II) were ruled out due to the observation of n.m.r. spectra indicating equivalent cyclopentadienyl rings and R groups for the two known isomers.[2] These isomers were originally reported [2,3] to have one carbonyl band in their i.r. spectrum, but later studies [4] have confirmed that one isomer has two such bands. Moreover, the ' unstable ' isomer having two bands is converted on heating into the ' stable ' one-band isomer, the reverse process being effected by u.v. irradiation.[2-4] The ' stable ' isomer of $[\{Fe(CO)(\mu\text{-}SPh)(\eta\text{-}C_5H_5)\}_2]$ was shown [5] to have a *cis*-(I)-type structure by *X*-ray diffraction and the ' unstable ' isomer proposed [2] to have the structure *cis*-(III). However, Haines *et al.*[4] suggested that the ' unstable ' two-band isomer was correctly formulated as *trans*-(I), on the grounds that the carbonyl band of the ' stable ' isomer is 20—40 cm^{-1} higher in energy that those of the ' unstable ' isomer, a trend which is observed for the structurally characterised *cis*- and *trans*-$[\{Fe(CO)(\mu\text{-}MR_2)(\eta\text{-}C_5H_5)\}_2]$ (M = P or As, R = Me or Ph).[6] The isolation of a third isomer of $[\{Fe(CO)(\mu\text{-}SPh)(\eta\text{-}C_5H_5)\}_2]$, thought to be of structure *cis*-(II) or *cis*-(III), has been reported.[4] Complexes $[\{Fe(CO)(\mu\text{-}EPh)(\eta\text{-}C_5H_5)\}_2]$ (E = Se or Te) are also known [7] and for selenium found to exist as two isomers analogous to those for sulphur.

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[1] Part 3, R. Goddard, S. D. Killops, S. A. R. Knox, and P. Woodward, *J.C.S. Dalton*, 1978, preceding paper.

[2] M. Ahmad, R. Bruce, and G. R. Knox, *J. Organometallic Chem.*, 1966, **6**, 1.

[3] M. Dekker, G. R. Knox, and C. G. Robertson, *J. Organometallic Chem.*, 1969, **18**, 161.

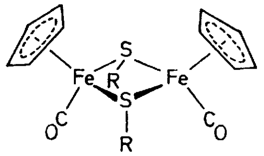
[4] R. J. Haines, J. A. DeBeer, and R. Greatrex, *J. Organometallic Chem.*, 1975, **85**, 89.

[5] G. Ferguson, C. Hannaway, and K. M. S. Islam, *Chem. Comm.*, 1968, 1165.

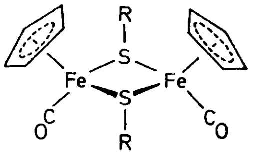
[6] R. G. Hayter, *J. Amer. Chem. Soc.*, 1963, **85**, 3120.

[7] E. D. Schermer and W. H. Baddley, *J. Organometallic Chem.*, 1971, **27**, 83.

In this paper we describe complexes $[\{Ru(CO)(\mu\text{-}ER)(\eta\text{-}C_5H_5)\}_2]$ (ER = SMe, SCH_2Ph, SPh, or SePh), the study of whose isomerism sheds considerable light on the iron analogues and has led to the identification [8] of the third 'isomer' of $[\{Fe(CO)(\mu\text{-}SPh)(\eta\text{-}C_5H_5)\}_2]$. Two complexes $[\{Ru(CO)(\mu\text{-}SR)(\eta\text{-}C_5H_5)\}_2]$ (R = Me or C_6F_5) have been previously described, obtained as mixtures of two isomers which were not separated.[9]



cis—(I)



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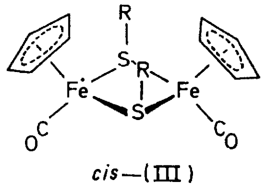

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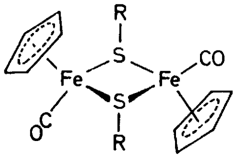
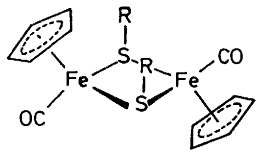


trans—(I)



trans—(II)

TABLE 1

Physical and spectroscopic data for the complexes

				^{1}H N.m.r. spectrum (τ) [b]	
Complex	Colour	M.p. (θ_c/°C)	Carbonyl-stretching bands (cm^{-1}) [a]	C_5H_5	R
$[Ru(CO)_2(SMe)(\eta\text{-}C_5H_5)]$	Yellow	55—56	2 039s, 1 987vs [c]	4.6 (s, 5)	8.0 (s, 3)
$[Ru(CO)_2(SCH_2Ph)(\eta\text{-}C_5H_5)]$	Orange	198—200	2 038s, 1 986vs [c]		
$[Ru(CO)_2(SR)(\eta\text{-}C_5H_5)]$ ($R = Bu^t/SBu^t$)	Orange	98—100	2 037s, 1 988s [c]	4.6 (s, 5)	8.8 (s, 9)
$[Ru(CO)_2(SPh)(\eta\text{-}C_5H_5)]$	Yellow	100—101	2 041s, 1 992vs [c]	4.67 (s, 5)	2.63 (m, 5)
$[Ru(CO)_2(SePh)(\eta\text{-}C_5H_5)]$	Red	205—206	2 035vs, 1 983s	See text	
cis-$[\{Ru(CO)(\mu\text{-}SMe)(\eta\text{-}C_5H_5)\}_2]$	Orange	168—170	1 959s	5.22 (s, 5)	7.93 (s, 3)
trans-$[\{Ru(CO)(\mu\text{-}SMe)(\eta\text{-}C_5H_5)\}_2]$	Red	134—136	1 948s, 1 934s	5.17 (s, 5)	7.83 (s, 3)
cis-$[\{Ru(CO)(\mu\text{-}SCH_2Ph)(\eta\text{-}C_5H_5)\}_2]$	Orange	172—173	1 954s	5.65 (s, 5)	2.9 (m, 5), 6.70 (s, 2)
trans-$[\{Ru(CO)(\mu\text{-}SCH_2Ph)(\eta\text{-}C_5H_5)\}_2]$	Red	181—182	1 954s, 1 945mw, 1 928mw, 1 916m	See Figures 1 and 2	
cis-$[Ru_2(CO)_2(\mu\text{-}SBu^t)(\mu\text{-}S_2Bu^t)(\eta\text{-}C_5H_5)_2]$	Orange	142—143	1 968s	5.23 (s, 10)	8.80 (s, 9), 8.90 (s, 9)
trans-$[Ru_2(CO)_2(\mu\text{-}SBu^t)(\mu\text{-}S_2Bu^t)(\eta\text{-}C_5H_5)_2]$	Red	130—131	1 948m, 1 935s	4.99 (s, 17), 5.07 (s, 10)	8.72 (s, 18), 8.75 (s, 30)
cis-$[\{Ru(CO)(\mu\text{-}SPh)(\eta\text{-}C_5H_5)\}_2]$	Orange	193—195	1 978s	5.0 (s, 5)	2.85 (m, 5)
trans-$[\{Ru(CO)(\mu\text{-}SPh)(\eta\text{-}C_5H_5)\}_2]$	Red	89—90	1 954s, 1 940s	5.42 (s, 5)	2.70 (m, 5)
cis-$[\{Ru(CO)(\mu\text{-}SePh)(\eta\text{-}C_5H_5)\}_2]$	Orange	195—196	1 976s	5.07 (s, 7), 5.43 (s, 3)	2.85 (m, 10)
trans-$[\{Ru(CO)(\mu\text{-}SePh)(\eta\text{-}C_5H_5)\}_2]$	Red	161—162	1 948s, 1 935s	See Figure 3	
$[Ru_3(CO)_2(SMe)_3(\eta\text{-}C_5H_5)_3]$	Red	175 (decomp.)	1 938s, 1 763m	5.07 (s, 10), 5.27 (s, 5)	7.34 (s, 3), 7.78 (s, 6)
$[Ru_3(CO)_2(SPh)_3(\eta\text{-}C_5H_5)_3]$	Red	140 (decomp.)	1 944s, 1 767m	5.35 (s, 7), 5.40 (s, 3), 5.43 (s, 2), 6.12 (s, 3)	2.65 (m, 15)

[a] In cyclohexane. [b] In $CDCl_3$; relative intensities are given in parentheses. [c] In hexane.

RESULTS AND DISCUSSION

Unlike $[\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$,[2,4] the reactions of $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2]$ with disulphides S_2R_2 (R = Me, Bu^t, CH_2Ph, or Ph) or Se_2Ph_2 proceed only under u.v. irradiation. For other than $S_2Bu^t{}_2$, complexes $[Ru(CO)_2(ER)(\eta\text{-}C_5H_5)]$ and $[\{Ru(CO)(\mu\text{-}ER)(\eta\text{-}C_5H_5)\}_2]$ (ER = SMe, SCH_2Ph, SPh, or SePh) are formed, clearly identified by i.r., mass, and ^1H n.m.r. spectra and analytical data (Tables 1 and 2). With $S_2Bu^t{}_2$ the products are an inseparable mixture of $[Ru(CO)_2(SBu^t)(\eta\text{-}C_5H_5)]$ and $[Ru(CO)_2(S_2Bu^t)(\eta\text{-}C_5H_5)]$, together with $[Ru_2(CO)_2(\mu\text{-}SBu^t)(\mu\text{-}S_2Bu^t)(\eta\text{-}C_5H_5)_2]$. Under irradiation at room temperature the mononuclear ruthenium complexes are in general favoured, while irradiation of refluxing toluene solutions of reactants yields almost exclusively the diruthenium complexes (Table 3).

There are two possible sources of the extra sulphur atom observed in the products of treating $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2]$ with $S_2Bu^t{}_2$. First, the disulphide was known to contain a very small amount of Bu^tSSSBu^t as impurity, which would readily provide the $^{\bullet}S_2Bu^t$ radical on irradiation. However, this radical could also be produced from $S_2Bu^t{}_2$ by even the relatively long-wavelength u.v. radiation (filtered through Pyrex) employed in this work. For primary and secondary dialkyl disulphides, short-wavelength u.v. radiation is required for C–S bond cleavage, but if stabilised carbon radicals can be generated, as is the case with tertiary dialkyl disulphides such as $S_2Bu^t{}_2$, C–S fission is competitive with S–S fission at long wavelengths.[10]

As expected, heating or irradiating solutions of

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[8] S. D. Killops, S. A. R. Knox, G. H. Riding, and A. J. Welch, *J.C.S. Chem. Comm.*, 1978, 486.

[9] G. R. Knox and A. Pryde, *J. Organometallic Chem.*, 1974, **74**, 105.

[10] T. D. Coyle, *Chem. Soc. Rev.*, 1975, **4**, 523.

$[\mathrm{Ru(CO)_2(ER)(\eta\text{-}C_5H_5)}]$ (ER = SMe, $\mathrm{SCH_2Ph}$, $\mathrm{SBu^t/S_2Bu^t}$, or SePh) gave chiefly the appropriate diruthenium complex (Table 4). Slow ' dimerisation ' also occurred in the solid state at room temperature when ER = SMe or SePh, being complete within days. The selenium complex is converted rapidly in solution even at room temperature and an n.m.r. spectrum could not be recorded. Irradiation of $[\mathrm{Ru(CO)_2(ER)(\eta\text{-}C_5H_5)}]$ (ER = SMe or SPh) gave as a minor product a red crystalline complex $[\mathrm{Ru_3(CO)_2(SR)_3(\eta\text{-}C_5H_5)_3}]$ (1). The methyl derivative has been described previously[9] and assigned a structure (2) on the basis of terminal and bridging carbonyl bands observed in the i.r., with two cyclopentadienyl and two SMe signals in the ^{1}H n.m.r. spectrum, each pair of relative intensity 2 : 1. The presence of a terminal SR ligand seems unlikely, however, and we favour structure (1), which also accords with these data. The phenylthio-complex equally has both terminal and bridging carbonyl absorptions in the i.r., but there are four cyclopentadienyl n.m.r. signals of differing intensity (Table 1), indicating the presence of isomers, perhaps as a result of variable

TABLE 2

Analytical and mass-spectral data for the complexes

Complex	Analysis (%)[a] C	H	S	*M*[a]
$[\mathrm{Ru(CO)_2(SMe)(\eta\text{-}C_5H_5)}]$	35.8 (35.7)	3.0 (3.0)	12.0 (11.9)	270 (270)
$[\mathrm{Ru(CO)_2(SCH_2Ph)(\eta\text{-}C_5H_5)}]$	47.5 (48.7)	4.8 (3.5)		346 (346)
$[\mathrm{Ru(CO)_2(SR)(\eta\text{-}C_5H_5)}]$ (R = $\mathrm{Bu^t/SBu^t}$)	40.5 (38.5)	4.4 (4.1)		344 (344)[b]
$[\mathrm{Ru(CO)_2(SPh)(\eta\text{-}C_5H_5)}]$	47.2 (47.1)	3.2 (3.0)	10.3 (9.7)	332 (332)
cis-$[\{\mathrm{Ru(CO)(\mu\text{-}SMe)(\eta\text{-}C_5H_5)}\}_2]$	only small amount hand-separated			483 (483)
trans-$[\{\mathrm{Ru(CO)(\mu\text{-}SMe)(\eta\text{-}C_5H_5)}\}_2]$				483 (483)
cis-$[\{\mathrm{Ru(CO)(\mu\text{-}SCH_2Ph)(\eta\text{-}C_5H_5)}\}_2]$	49.3 (49.2)	3.9 (3.8)	11.1 (10.1)	635 (635)
trans-$[\{\mathrm{Ru(CO)(\mu\text{-}SCH_2Ph)(\eta\text{-}C_5H_5)}\}_2]$	48.8 (49.2)	4.1 (3.8)	10.4 (10.1)	635 (635)
cis-$[\mathrm{Ru_2(CO)_2(\mu\text{-}SBu^t)(\mu\text{-}S_2Bu^t)(\eta\text{-}C_5H_5)_2}]$	39.4 (40.1)	4.8 (4.7)	13.3 (16.6)	599 (599)
trans-$[\mathrm{Ru_2(CO)_2(\mu\text{-}SBu^t)(\mu\text{-}S_2Bu^t)(\eta\text{-}C_5H_5)_2}]$				599 (599)
cis-$[\{\mathrm{Ru(CO)(\mu\text{-}SPh)(\eta\text{-}C_5H_5)}\}_2]$	47.3 (47.5)	3.6 (3.3)	10.1 (10.6)	607 (607)
trans-$[\{\mathrm{Ru(CO)(\mu\text{-}SPh)(\eta\text{-}C_5H_5)}\}_2]$	47.8 (47.5)	4.0 (3.3)	10.3 (10.6)	607 (607)
cis-$[\{\mathrm{Ru(CO)(\mu\text{-}SePh)(\eta\text{-}C_5H_5)}\}_2]$	40.4 (41.2)	3.3 (2.9)		701 (701)
trans-$[\{\mathrm{Ru(CO)(\mu\text{-}SePh)(\eta\text{-}C_5H_5)}\}_2]$	41.1 (41.2)	2.9 (2.9)		701 (701)
$[\mathrm{Ru_3(CO)_2(SMe)_3(\eta\text{-}C_5H_5)_3}]$				697 (697)
$[\mathrm{Ru_3(CO)_2(SPh)_3(\eta\text{-}C_5H_5)_3}]$	47.4 (47.7)	3.7 (3.4)	11.2 (10.9)	Involatile

[a] Calculated values are given in parentheses. [b] For $[\mathrm{Ru(CO)_2(S_2Bu^t)(\eta\text{-}C_5H_5)}]$ (heaviest ion).

TABLE 3

Irradiation of $[\{\mathrm{Ru(CO)_2(\eta\text{-}C_5H_5)}\}_2]$ (1 mmol)–$\mathrm{E_2R_2}$

		Chromatography		Yield *	
$\mathrm{E_2R_2}$	Product	$\mathrm{CH_2Cl_2}$–hexane eluant	Band colour	Room temperature	Reflux
$\mathrm{S_2Me_2}$	*cis*- and *trans*-$[\{\mathrm{Ru(CO)(\mu\text{-}SMe)(\eta\text{-}C_5H_5)}\}_2]$	1 : 3	Orange	Trace	0.2 g (21)
(1.34 g, 14 mmol)	$[\mathrm{Ru(CO)_2(SMe)(\eta\text{-}C_5H_5)}]$	2 : 3	Yellow	0.11 g (20)	0
$\mathrm{S_2(CH_2Ph)_2}$	*trans*-$[\{\mathrm{Ru(CO)(\mu\text{-}SCH_2Ph)(\eta\text{-}C_5H_5)}\}_2]$	1 : 3	Yellow	32 mg (5)	Trace
(1.5 g, 6 mmol)	*cis*-$[\{\mathrm{Ru(CO)(\mu\text{-}SCH_2Ph)(\eta\text{-}C_5H_5)}\}_2]$	1 : 3	Orange	0	5 mg (1)
	$[\mathrm{Ru(CO)_2(SCH_2Ph)(\eta\text{-}C_5H_5)}]$	2 : 3	Yellow	20 mg (3)	0
$\mathrm{S_2Bu^t{}_2}$	*trans*-$[\mathrm{Ru_2(CO)_2(\mu\text{-}SBu^t)(\mu\text{-}S_2Bu^t)(\eta\text{-}C_5H_5)_2}]$	1 : 9	Yellow	Trace	6 mg (1)
(1.82 g, 10 mmol)	*cis*-$[\mathrm{Ru_2(CO)_2(\mu\text{-}SBu^t)(\mu\text{-}S_2Bu^t)(\eta\text{-}C_5H_5)_2}]$	1 : 9	Orange	2 mg (<1)	0.13 g (15)
	$[\mathrm{Ru(CO)_2(ER)(\eta\text{-}C_5H_5)}]$ (ER = $\mathrm{SBu^t/S_2Bu^t}$)	1 : 9	Yellow	20 mg (6)	0
$\mathrm{S_2Ph_2}$	*trans*-$[\{\mathrm{Ru(CO)(\mu\text{-}SPh)(\eta\text{-}C_5H_5)}\}_2]$	1 : 9	Orange	23 mg (4)	0.12 g (19)
(1.5 g, 7 mmol)	*cis*-$[\{\mathrm{Ru(CO)(\mu\text{-}SPh)(\eta\text{-}C_5H_5)}\}_2]$	1 : 9	Orange	85 mg (14)	0.31 g (51)
	$[\mathrm{Ru(CO)_2(SPh)(\eta\text{-}C_5H_5)}]$	1 : 6	Yellow	0.2 g (31)	0
$\mathrm{Se_2Ph_2}$	*trans*-$[\{\mathrm{Ru(CO)(\mu\text{-}SePh)(\eta\text{-}C_5H_5)}\}_2]$	1 : 9	Red	0.14 g (20)	
(2.0 g, 6 mmol)	*cis*-$[\{\mathrm{Ru(CO)(\mu\text{-}SePh)(\eta\text{-}C_5H_5)}\}_2]$	1 : 9	Yellow	Trace	
	$[\mathrm{Ru(CO)_2(SePh)(\eta\text{-}C_5H_5)}]$	1 : 9	Orange	0.34 g (45)	

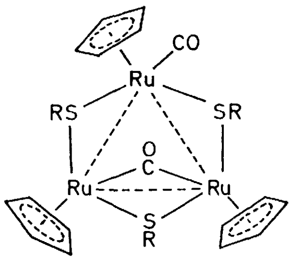
* Percentages are given in parentheses.

TABLE 4

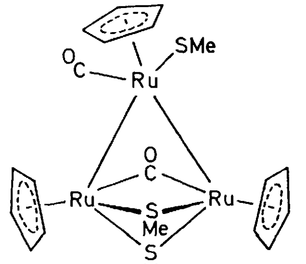
' Dimerisation ' of $[\mathrm{Ru(CO)_2(SR)(\eta\text{-}C_5H_5)}]$

		Chromatography		Yield (%)	
R	Product	$\mathrm{CH_2Cl_2}$–hexane eluant	Band colour	Reflux	U.v.
Me	*cis*- and *trans*-$[\{\mathrm{Ru(CO)(\mu\text{-}SMe)(\eta\text{-}C_5H_5)}\}_2]$	1 : 4	Orange	75	70
	$[\mathrm{Ru_3(CO)_2(SMe)_3(\eta\text{-}C_5H_5)_3}]$	1 : 1	Red	0	5
$\mathrm{CH_2Ph}$	*cis*-$[\{\mathrm{Ru(CO)(\mu\text{-}SCH_2Ph)(\eta\text{-}C_5H_5)}\}_2]$	1 : 3	Orange	90	
$\mathrm{Bu^t/SBu^t}$	*trans*-$[\mathrm{Ru_2(CO)_2(\mu\text{-}SBu^t)(\mu\text{-}S_2Bu^t)(\eta\text{-}C_5H_5)_2}]$	1 : 9	Orange-red	Trace	
	cis-$[\mathrm{Ru_2(CO)_2(\mu\text{-}SBu^t)(\mu\text{-}S_2Bu^t)(\eta\text{-}C_5H_5)_2}]$	1 : 9	Orange	80	
Ph	*trans*-$[\{\mathrm{Ru(CO)(\mu\text{-}SPh)(\eta\text{-}C_5H_5)}\}_2]$	1 : 6	Orange-red	20	22
	cis-$[\{\mathrm{Ru(CO)(\mu\text{-}SPh)(\eta\text{-}C_5H_5)}\}_2]$	1 : 6	Orange	50	0
	$[\mathrm{Ru_3(CO)_2(SPh)_3(\eta\text{-}C_5H_5)_3}]$	2 : 1	Red	0	68

phenyl-group orientation. These trinuclear ruthenium species can be compared with the complexes $[Fe_3(CO)_2(\mu_3\text{-}S)(\mu_3\text{-}SR)(\eta\text{-}C_5H_5)_3]$ formed in the reactions of $[\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ with S_2R_2.[4]



(1)

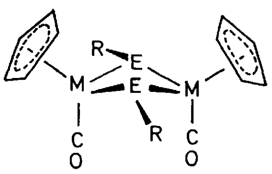


(2)

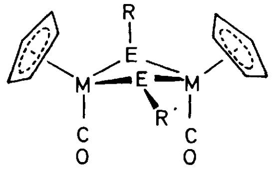
The diruthenium complexes $[\{Ru(CO)(\mu\text{-}ER)(\eta\text{-}C_5H_5)\}_2]$ (ER = SMe, SCH_2Ph, SPh, or SePh) and $[Ru_2(CO)_2(\mu\text{-}SBu^t)(\mu\text{-}S_2Bu^t)(\eta\text{-}C_5H_5)_2]$ are more prone to isomerism than are the iron complexes of this type. For $[\{Fe(CO)(\mu\text{-}SR)(\eta\text{-}C_5H_5)\}_2]$ one isomer is observed when R = Bu^t or CH_2Ph and two when R = Me, Et, Pr^i, Bu^n, or Ph,[4] one isomer displaying a single carbonyl band in the i.r. and the other two such bands. These were assigned[4] structures *cis*-(I) and *trans*-(I) respectively, as outlined earlier. The diruthenium complexes are readily separated into what appear to be two analogous isomers, *viz.* an orange form having one carbonyl band and a red form having two bands. Closer inspection reveals, however, that in some cases these ' isomers ' are an inseparable mixture of isomers arising from a multiplicity of R-group orientation superimposed on a gross *cis* or *trans* isomerism of the two cyclopentadienyl ligands with respect to the Ru_2E_2 (E = S or Se) ring.

It is proposed, for reasons identical to those outlined in the introduction for iron, that isomers of $[\{Ru(CO)(\mu\text{-}ER)(\eta\text{-}C_5H_5)\}_2]$ displaying one and two carbonyl i.r. bands have structures with *cis* and *trans* arrangements of the cyclopentadienyl rings respectively. At first sight this appears at odds with the fact that such *cis* and *trans* isomers are predicted to have two and one i.r.-active carbonyl bands respectively, but this presumes that the Ru_2E_2 ring is planar. When the ring is assumed to be folded, as has been determined crystallographically for *cis*-$[\{Fe(CO)(\mu\text{-}SPh)(\eta\text{-}C_5H_5)\}_2]$,[5] the anticipated numbers of carbonyl bands are consistent with those observed. The folding of an M_2E_2 ring as in *cis*-$[\{Fe(CO)(\mu\text{-}SPh)(\eta\text{-}C_5H_5)\}_2]$ brings the two CO groups into nearly parallel alignment, shown for the *cis*-isomers (3)—(5), and only the symmetric stretching of the two groups will therefore generate an i.r. band of significant intensity. Conversely, similar folding of the ring in the *trans* isomers (6)—(8) draws the two CO groups out of alignment and leads to two stretching modes of appreciable intensity. The assignment of *cis* and *trans* geometry to isomers having one and two carbonyl bands on grounds other than their i.r. spectra therefore demands the conclusion that the M_2E_2 rings of complexes $[\{M(CO)(\mu\text{-}ER)(\eta\text{-}C_5H_5)\}_2]$ (M = Fe or Ru, E = S or Se) are appreciably non-planar.

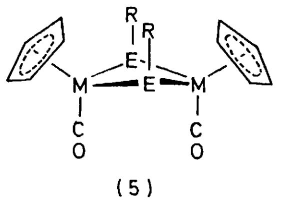
Both the non-planarity of M_2E_2 rings and relative stabilities (discussed below) of *cis* and *trans* isomers can usefully be considered in terms of steric effects. For a *cis* isomer the folding of the ring as illustrated reduces clash of the cyclopentadienyl rings while not substantially increasing the other significant intramolecular interactions, *i.e.* those between R $\cdots$ R and R $\cdots$ C_5H_5 groups. Folding of the ring in the other sense about the E $\cdots$ E axis brings an unacceptable interaction of the cyclopentadienyl rings and is not considered further. There are therefore three plausible *cis* isomers (3)—(5) arising from lone-pair and R-group orientational variations. Of these (3) is clearly most favoured in terms of R $\cdots$ R and R $\cdots$ C_5H_5 interactions and (5) least favoured, with (4) in between. In support of these assertions the *cis* isomer of $[\{Fe(CO)(\mu\text{-}SPh)(\eta\text{-}C_5H_5)\}_2]$[5] adopts the arrangement (3).



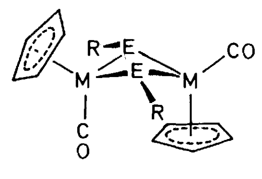
(3)



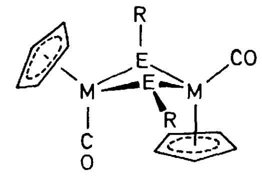
(4)



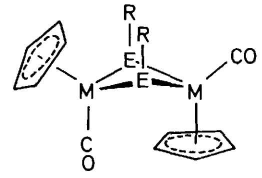
(5)



(6)

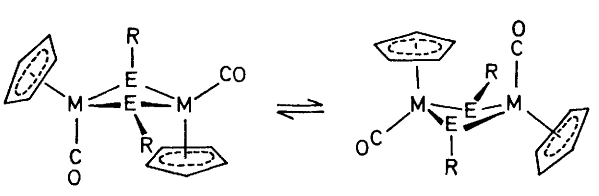


(7)



(8)

There are three possible *trans* isomers (6)—(8) with a non-planar M_2E_2 ring, whose relative stabilities will be controlled by R $\cdots$ R and R $\cdots$ C_5H_5 interactions. A low stability for (8) can therefore be anticipated as a result of severe R $\cdots$ R clash, but neither (6) nor (7) appears clearly favoured. In practise, the n.m.r. spectra of *trans* isomers of $[\{Fe(CO)(\mu\text{-}SR)(\eta\text{-}C_5H_5)\}_2]$



(7a) (7b)

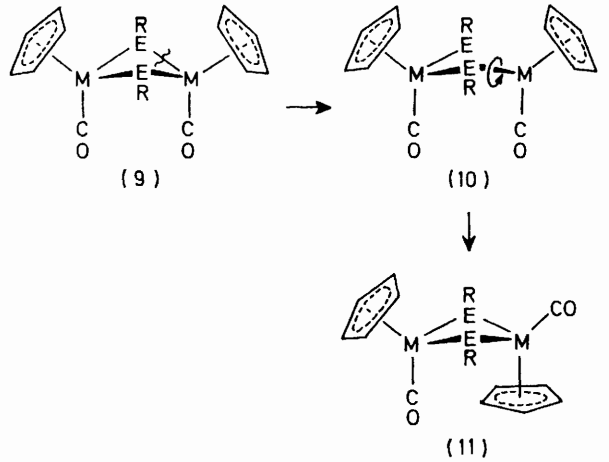
reveal equivalence of the cyclopentadienyl and R groups, consistent with an arrangement (7) which is undergoing ready ring inversion (7a) $\rightleftharpoons$ (7b).[4] The existence of such a low-energy ring inversion has been established in complexes $[\{Rh(\mu\text{-}SR)(\eta^4\text{-}L)\}_2]$ (L = cyclo-octatetraene or cyclo-octa-1,5-diene), which contain similarly folded and non-metal–metal bonded Rh_2S_2 rings.[11]

While (3) is the favoured configuration of *cis*-$[\{Fe(CO)(\mu\text{-}SR)(\eta\text{-}C_5H_5)\}_2]$ and (7) of the *trans* isomer, overall *cis* is thermodynamically more stable that *trans*, *trans* to *cis* conversion being achieved thermally and the reverse process by u.v. irradiation.[2,4] This is understandable in terms of steric effects. Allowing a folded Fe_2S_2 ring, $C_5H_5 \cdots C_5H_5$ and $R \cdots R$ interactions appear insignificant for either *cis* or *trans*, but this is not so for $R \cdots C_5H_5$ interaction which is clearly less in (3) than in (7). Support for the importance of this interaction is provided by the non-existence of *trans*-$[\{Fe(CO)(\mu\text{-}SR)(\eta\text{-}C_5H_5)\}_2]$ for bulky t-butyl and benzyl groups.[4] In either *cis* or *trans* isomers, R groups can dispose themselves well apart [(3) or (6)], but only in a *cis* isomer can they avoid interaction with cyclopentadienyl ligands.

For $[\{Ru(CO)(\mu\text{-}ER)(\eta\text{-}C_5H_5)\}_2]$ the stability distinction between *cis* and *trans* isomers is not so marked, in accord with the expected reduced role of steric effects for complexes of ruthenium, *cf.* iron. When ER = SMe, SBu^t/S_2Bu^t, or SCH_2Ph the same pattern as for iron is shown, *i.e. trans* converted into *cis* thermally and *cis* into *trans* on u.v. irradiation. For $[\{Ru(CO)(\mu\text{-}SPh)(\eta\text{-}C_5H_5)\}_2]$, however, the *trans* isomer is clearly the more stable, being unaffected by heat or irradiation, conditions which effect complete *cis* to *trans* isomerisation. A greater stability of *trans* isomers for ruthenium is also shown by heating *trans*-$[\{Ru(CO)(\mu\text{-}SePh)(\eta\text{-}C_5H_5)\}_2]$, when only partial conversion into the *cis* form can be achieved.

Several experiments on ' dimerisation ' of $[Ru(CO)_2(ER)(\eta\text{-}C_5H_5)]$ also bear out the relative isomer stabilities described above (Table 4). Thus, heating $[Ru(CO)_2(SCH_2Ph)(\eta\text{-}C_5H_5)]$ in toluene gave only *cis*-$[\{Ru(CO)(\mu\text{-}SCH_2Ph)(\eta\text{-}C_5H_5)\}_2]$, while irradiation of $[Ru(CO)_2(SPh)(\eta\text{-}C_5H_5)]$ yielded *trans*-$[\{Ru(CO)(\mu\text{-}SPh)(\eta\text{-}C_5H_5)\}_2]$ exclusively. Significantly, reflux of $[Ru(CO)_2(SePh)(\eta\text{-}C_5H_5)]$ in toluene gave initially only *cis*-$[\{Ru(CO)(\mu\text{-}SePh)(\eta\text{-}C_5H_5)\}_2]$, as a product of kinetic control, which on prolonged heating was converted into the thermodynamically favoured *trans* form.

The barriers to *cis* $\rightleftharpoons$ *trans* isomerisation of $[\{M(CO)(\mu\text{-}ER)(\eta\text{-}C_5H_5)\}_2]$ are evidently relatively high when compared with those associated with the similar isomerisations of $[\{M(CO)(\mu\text{-}CO)(\eta\text{-}C_5H_5)\}_2]$[12] and of $[(\eta\text{-}C_5H_5)(OC)Fe(\mu\text{-}CO)(\mu\text{-}GeMe_2)Fe(CO)(\eta\text{-}C_5H_5)]$.[13] Each of these complexes has been proposed to isomerise *via* a non-bridged intermediate, the higher barrier for the latter reflecting a low tendency for $GeMe_2$ to become a terminal ligand. The *cis* $\rightleftharpoons$ *trans* isomerisation of $[\{M(CO)(\mu\text{-}ER)(\eta\text{-}C_5H_5)\}_2]$ could proceed somewhat similarly, by a partial dissociation of the molecule (9) $\longrightarrow$ (10) $\longrightarrow$ (11), or by a dissociation–recombination path involving 16-electron $[M(CO)(ER)(\eta\text{-}C_5H_5)]$ fragments. Evidence for the co-existence of each process has been obtained by Dekker *et al.*,[3] who observed that heating ' unstable ' *trans*-$[\{Fe(CO)(\mu\text{-}SPh)(\eta\text{-}C_5H_5)\}_2]$ and *trans*-$[\{Fe(CO)(\mu\text{-}SC_6H_4Me)(\eta\text{-}C_5H_5)\}_2]$ together in benzene gave predominantly the respective ' stable ' *cis* isomers and a low yield of *cis*-$[Fe_2(CO)_2(\mu\text{-}SPh)(\mu\text{-}SC_6H_4Me)(\eta\text{-}C_5H_5)_2]$. The proportion of ' scrambled ' product was lowered further at increased dilution of reactants, thus minimising the importance of the dissociation–recombination path.



The *cis* and *trans* forms of $[\{Ru(CO)(\mu\text{-}ER)(\eta\text{-}C_5H_5)\}_2]$ appear, like iron, to favour the arrangements (3) and (7), but not to the total exclusion of the other R-group orientations. Only for ER = SMe or SPh are there single *cis* and *trans* isomers; for ER = SCH_2Ph and for $[Ru_2(CO)_2(\mu\text{-}SBu^t)(\mu\text{-}S_2Bu^t)(\eta\text{-}C_5H_5)_2]$ there are one *cis* and two *trans*, and for ER = SePh two *cis* and two *trans* isomers. This proliferation is another indication of lower steric control of configuration in the complexes $[\{Ru(CO)(\mu\text{-}ER)(\eta\text{-}C_5H_5)\}_2]$ compared with $[\{Fe(CO)(\mu\text{-}SR)(\eta\text{-}C_5H_5)\}_2]$.

In contrast to the *cis* $\rightleftharpoons$ *trans* isomerisation of $[\{Ru(CO)(\mu\text{-}ER)(\eta\text{-}C_5H_5)\}_2]$, interconversion of isomers varying only in R-group orientation may be opposed by low barriers and can occur on the n.m.r. time scale. For $[\{Ru(CO)(\mu\text{-}ER)(\eta\text{-}C_5H_5)\}_2]$ (ER = SMe or SPh) this situation does not arise since the complexes exist as a single *cis* isomer (3) and a single *trans* isomer (7), the latter undergoing the ready ring inversion (7a) $\rightleftharpoons$ (7b). No observation of the static form (7) was possible, even on recording the n.m.r. spectrum of *trans*-$[\{Ru(CO)(\mu\text{-}SPh)(\eta\text{-}C_5H_5)\}_2]$ at -100 °C. For $[Ru_2(CO)_2(\mu\text{-}SBu^t)(\mu\text{-}S_2Bu^t)(\eta\text{-}C_5H_5)_2]$ there exists only a single *cis* isomer (3), but there are two inseparable *trans* isomers. However, although the abundance of the last two

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[11] R. Hill, B. A. Kelly, F. G. Kennedy, S. A. R. Knox, and P. Woodward, *J.C.S. Chem. Comm.*, 1977, 434.

[12] J. G. Bullitt, F. A. Cotton, and T. J. Marks, *Inorg. Chem.*, 1972, **11**, 671.

[13] R. D. Adams, M. D. Brice, and F. A. Cotton, *Inorg. Chem.*, 1974, **13**, 1080.

varies with solvent, in a particular solvent their proportion is independent of temperature (25—90 °C in C_6H_5Cl), indicating a high barrier to isomerisation. The overlapping of signals in the n.m.r. spectrum precludes firm identification of the two isomers, but (6) and (7) are most likely for reasons discussed earlier.

It is the complexes $[\{Ru(CO)(\mu\text{-}ER)(\eta\text{-}C_5H_5)\}_2]$ (ER = SCH_2Ph or SePh) which show evidence of stereochemical non-rigidity on an n.m.r. time scale. The benzyl complex exists as a single *cis* isomer (3), but there are two inseparable *trans* isomers, evidenced by the i.r. spectrum. Their ^1H n.m.r. spectrum (Figure 1) shows that at −60 °C these are not interconverted. The spectrum is consistent with the presence of one isomer with inequivalent cyclopentadienyl rings (*a,a'*) and another less-abundant isomer with equivalent rings (*b*). The former is proposed to have configuration (6), on the grounds that the other possibility (8) has unacceptedly crowded benzyl groups, and the latter to have configuration (7). Again, ring inversion (7a) $\rightleftharpoons$ (7b) generates the single signal *b* observed for the C_5H_5 rings of this isomer, which falls appropriately near the average chemical shift of the *a,a'* signals of the other isomer. On warming to > −60 °C, collapse and coalescence of the cyclopentadienyl ring signals occurs and also of the methylenic benzyl proton signals. At >55 °C (Figure 2) sharpening of the signals continues until at 110 °C singlets are observed for the C_5H_5 and CH_2Ph protons. These changes are interpreted as being a consequence of a rapid interconversion of the *trans* forms (6) and (7), the mechanism of which is discussed later.

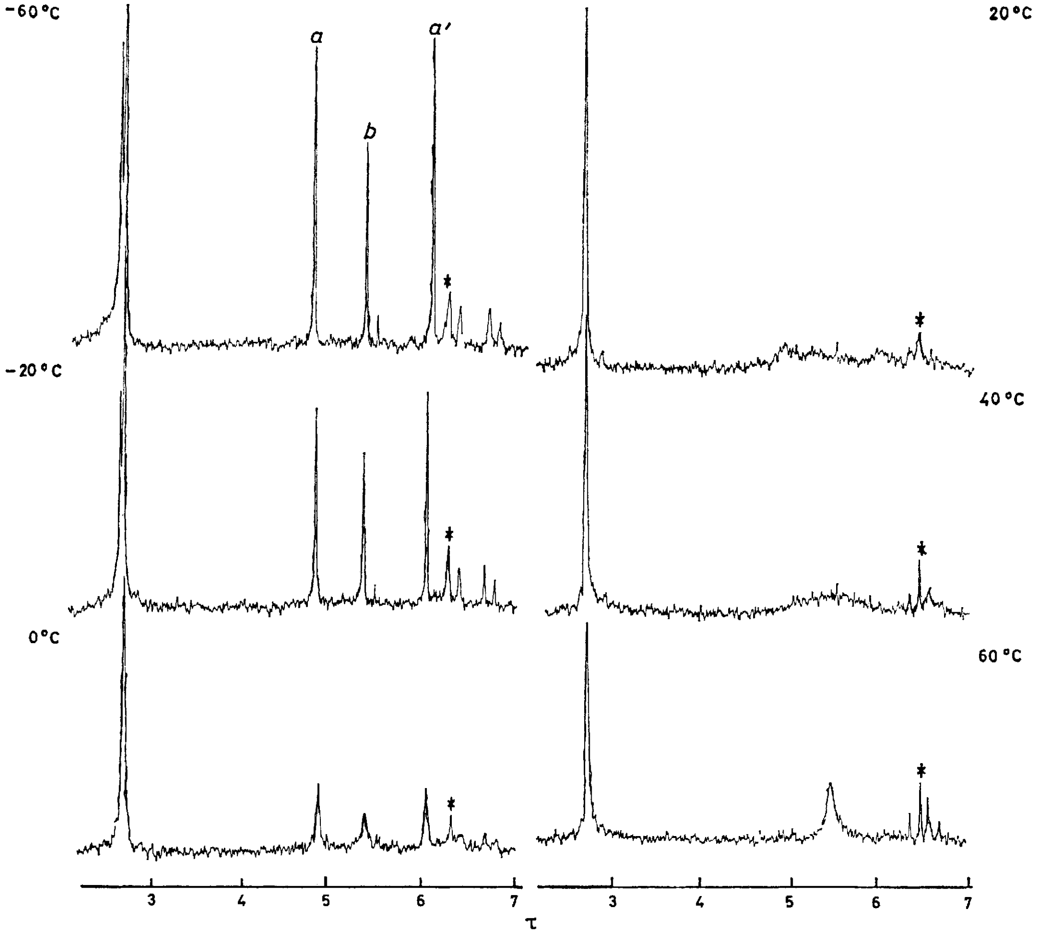


FIGURE 1 Hydrogen-1 n.m.r. spectrum of *trans*-$[\{Ru(CO)(\mu\text{-}SCH_2Ph)(\eta\text{-}C_5H_5)\}_2]$ in $CDCl_3$ solution. The asterisk indicates an impurity band

Both the *cis* and *trans* forms of $[\{Ru(CO)(\mu\text{-}SePh)(\eta\text{-}C_5H_5)\}_2]$ occur as mixtures of isomers arising from variation of the phenyl-group orientation on selenium. The ^1H n.m.r. spectrum of the inseparable *cis* isomers shows two sharp cyclopentadienyl signals in the ratio 7 : 3 at 25 °C in chlorobenzene which broaden on warming, coalesce, and reappear as a sharp singlet at 90 °C. A rapid interconversion of *cis* forms (3) and (4) is indicated, for each of which only one cyclopentadienyl resonance is expected.

The two *trans* forms of $[\{Ru(CO)(\mu\text{-}SePh)(\eta\text{-}C_5H_5)\}_2]$ are clearly analogous to those of $[\{Ru(CO)(\mu\text{-}SCH_2Ph)(\eta\text{-}C_5H_5)\}_2]$, the ^1H n.m.r. spectrum of the former at −20 °C (Figure 3) being similar to that of the latter at −60 °C (Figure 1). However, isomer (7) is here predominant, the (6) : (7) ratio of 1 : 2 contrasting with one of 3.4 : 1 for the benzyl complex. At higher temperatures the n.m.r.

spectrum shows the consequences of (6) $\rightleftharpoons$ (7) interconversion.

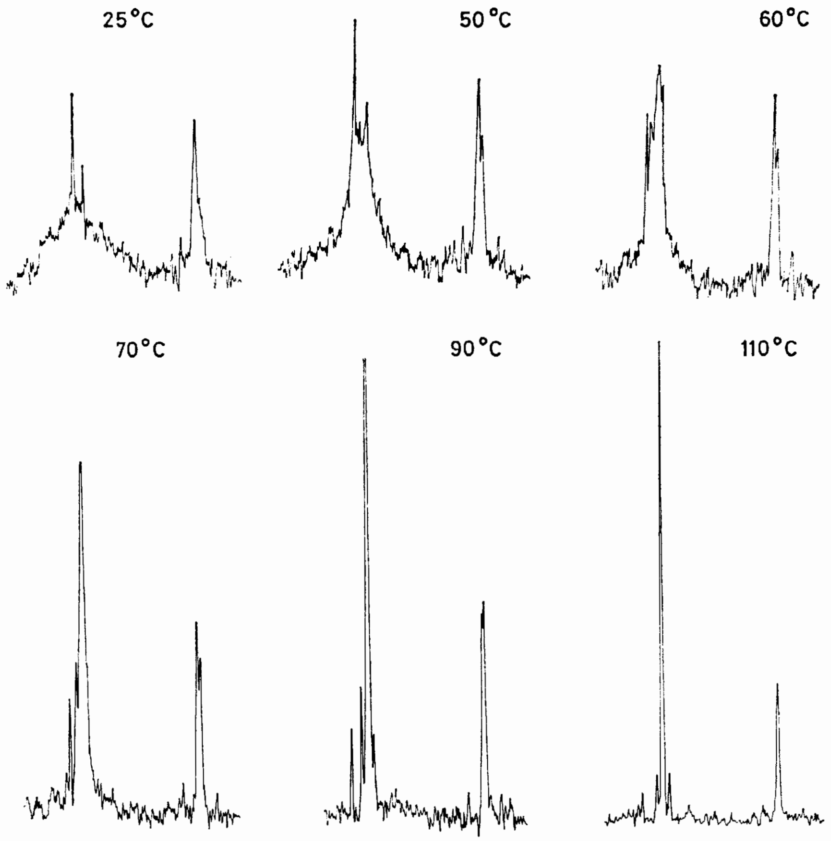
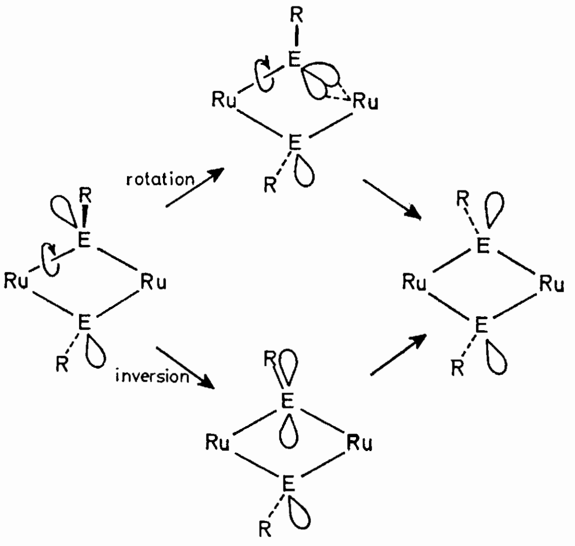


FIGURE 2 Hydrogen-1 n.m.r. spectrum of *trans*-[{Ru(CO)(μ-SCH$_2$Ph)(η-C$_5$H$_5$)}$_2$] in [^{2}H$_8$]toluene solution in the range τ 5—7

The isomerisations (3) $\rightleftharpoons$ (4) of *cis*-[{Ru(CO)(μ-SePh)(η-C$_5$H$_5$)}$_2$] and (6) $\rightleftharpoons$ (7) of *trans*-[{Ru(CO)(μ-ER)(η-C$_5$H$_5$)}$_2$] (ER = SCH$_2$Ph or SePh) are closely related, each involving a *syn* $\rightleftharpoons$ *anti* interchange of R-group environments while maintaining the relative C$_5$H$_5$ ligand orientation. A dissociative mechanism for this process can be discarded immediately, since this would effect *cis* $\rightleftharpoons$ *trans* isomerisation. The mechanism must therefore be intramolecular and two possibilities are depicted in the Scheme. That designated 'rotation' derives from Turley and Haake's early work [14] on dialkyl sulphide complexes of platinum and features an intramolecular displacement of one chalcogen electron pair from ruthenium by another *via* a rotation about an Ru–E bond. The other process, designated 'inversion', is exactly that: inversion at sulphur or selenium with the classical planar transition state and *p* orbital, which may be involved in bonding with the transition-metal atoms. In fact, these mechanisms represent two formalisms for describing what is in effect a chalcogen inversion and, as Abel *et al.*[15] have pointed out in connection with inversion in complexes of the type [PtCl$_2${S(CH$_2$SiMe$_3$)$_2$}$_2$], choice between the two is a matter of personal preference.



SCHEME Possible paths of isomerisation for (3) $\rightleftharpoons$ (4) and (6) $\rightleftharpoons$ (7)

Confirmation that the isomerisations under discussion proceed *via* inversion of a bridging chalcogen atom is provided by the n.m.r. spectrum of *trans*-[{Ru(CO)(μ-SCH$_2$Ph)(η-C$_5$H$_5$)}$_2$]. The pyramidal bridging sulphur atoms of the two isomers (6) and (7) are chiral and thus the methylenic benzyl protons are magnetically in-

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[14] P. C. Turley and P. Haake, *J. Amer. Chem. Soc.*, 1967, **89**, 4617.

[15] E. W. Abel, G. W. Farrow, K. G. Orrell, and V. Sik, *J.C.S. Dalton*, 1977, 42.

equivalent, irrespective of the rate of rotation about the S–C bond, and comprise an AB spin system. The n.m.r. spectrum of *trans*-[{Ru(CO)(μ-SCH$_2$Ph)(η-C$_5$H$_5$)}$_2$] shows at −60 °C (Figure 1) one somewhat broadened AB quartet [partially obscured by an impurity signal (designated by an asterisk)] which is attributed to two closely adjacent AB quartets due to the presence of (6) and (7). At the fast-exchange limit (110 °C) full averaging of C$_5$H$_5$ and SCH$_2$Ph group environments is attained, but, more importantly, magnetic equivalence of the methylenic protons is apparent, a phenomenon directly attributable to an inversion of the sulphur atoms.

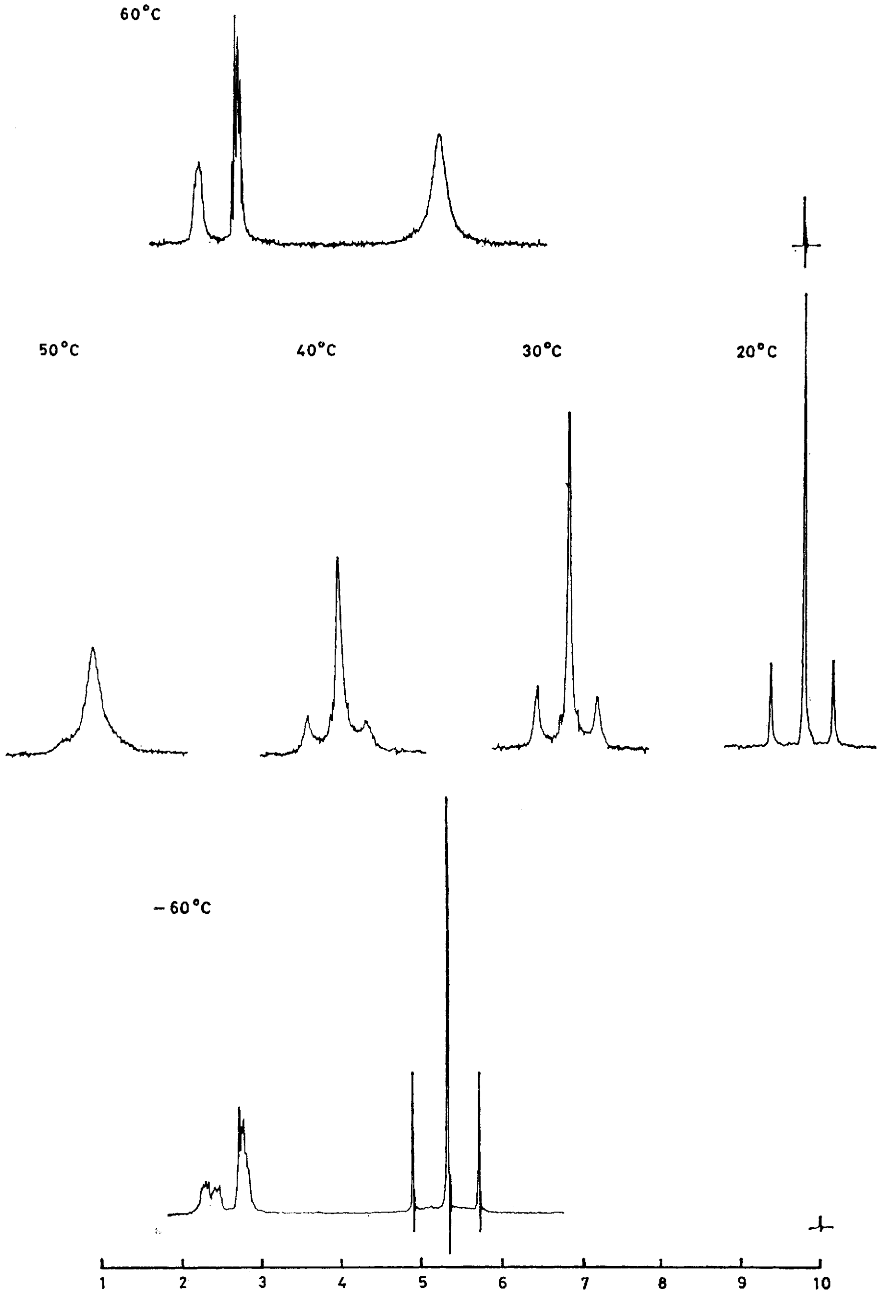


FIGURE 3 Hydrogen-1 n.m.r. spectrum of *trans*-[{Ru(CO)(μ-SePh)(η-C$_5$H$_5$)}$_2$] in CDCl$_3$ solution; spectra between 20 and 50 °C are of the τ 5—6 region only

The form of the methylenic proton n.m.r. signals of the isomers of [{Ru(CO)(μ-SCH$_2$Ph)(η-C$_5$H$_5$)}$_2$] establishes also that the earlier assignment of *cis* and *trans* configurations, primarily on the basis of i.r. spectra, was made correctly. As seen above, the bridging sulphur atoms of the *trans* form are chiral and the SC*H*$_2$Ph methylenic protons therefore appear as an AB spin system. The *cis* isomer, on the other hand, contains two ruthenium atoms in identical environments and the bridging sulphur atoms are not chiral. The methylenic hydrogens of such an isomer are consequently made magnetically equivalent by rotation about the S–C bond, as is observed for the isomer of $[\{Ru(CO)(\mu\text{-}SCH_2Ph)(\eta\text{-}C_5H_5)\}_2]$ with one carbonyl band in the i.r., previously designated *cis*.

Determination of the energy barriers associated with the (3) $\rightleftharpoons$ (4) and (6) $\rightleftharpoons$ (7) isomerisations sheds further light on the mechanism. For *cis*-$[\{Ru(CO)(\mu\text{-}SePh)(\eta\text{-}C_5H_5)\}_2]$ this is readily done since the two isomers each have a single cyclopentadienyl signal in the n.m.r. spectrum. Application of the relation (1),[16]

$$\Delta G^{\ddagger} = -RT_c\ln\left(\frac{2\pi \boldsymbol{h}\Delta\nu}{kT_c\{3[1 + 3^{\frac{1}{2}}(p_A - p_B)]\}^{\frac{1}{2}}}\right) \quad (1)$$

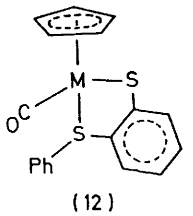
where $\Delta\nu$ is the separation of the signals at the slow-exchange limit, p_A and p_B are fractional populations of the two species, T_c is the coalescence temperature, and the other symbols have their usual significance, then provides $\Delta G^{\ddagger} = 70.2 \pm 1.0$ kJ mol^{-1} ($\Delta\nu$ 36 $\pm$ 2 Hz, T_c 338 $\pm$ 5 K, p_A 0.7, and p_B 0.3).

For the two *trans* isomers of $[\{Ru(CO)(\mu\text{-}SCH_2Ph)(\eta\text{-}C_5H_5)\}_2]$, relation (1) was applied to the coalescence of the equal-intensity cyclopentadienyl signals *a,a'* of Figure 1, making the assumption that this provides a measure of the barrier to (6) $\rightleftharpoons$ (7) isomerisation. The relatively low abundance of isomer (7) (*ca.* 1 : 3.4) makes this not unreasonable, the value obtained being $\Delta G^{\ddagger} = 58.7 \pm 1.0$ kJ mol^{-1} ($\Delta\nu$ 132 $\pm$ 2 Hz, T_c 303 $\pm$ 5 K, and $p_A = p_B = 0.5$). Application of the same procedure to *trans*-$[\{Ru(CO)(\mu\text{-}SePh)(\eta\text{-}C_5H_5)\}_2]$ can be seen from Figure 3 to be more tenuous, but provides $\Delta G^{\ddagger} = 66.4 \pm 1.0$ kJ mol^{-1} ($\Delta\nu$ 75 $\pm$ 2 Hz and T_c 323 $\pm$ 5 K).

Although it would be adventurous to place too great a weight on these values it is significant that they are of the order expected for inversion at sulphur or selenium and also that the value for sulphur is less than those for selenium, as expected. By way of comparison the free energies of activation for inversion in *trans*-$[PtCl_2(EEt_2)_2]$ are 58.4 $\pm$ 1.0 (E = S)[14] and 76.2 kJ mol^{-1} (E = Se)[17], and in *trans*-$[PdCl_2\{E(CH_2SiMe_3)_2\}_2]$ are 54.6 $\pm$ 0.1 (E = S)[15] and 69.3 $\pm$ 1.1 kJ mol^{-1} (E = Se).[15] It is concluded, therefore, that the stereochemical non-rigidity observed for *trans*-$[\{Ru(CO)(\mu\text{-}SCH_2Ph)(\eta\text{-}C_5H_5)\}_2]$ and for *cis*- and *trans*-$[\{Ru(CO)(\mu\text{-}SePh)(\eta\text{-}C_5H_5)\}_2]$ arises from single site inversion of sulphur or selenium.

In an attempt to obtain a complex analogous to $[Ru_2(CO)_2(\mu\text{-}SBu^t)(\mu\text{-}S_2Bu^t)(\eta\text{-}C_5H_5)_2]$, $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2]$ and S_2Ph_2 were subjected to u.v. irradiation in the presence of sulphur. No related complex was formed; instead formation of $[\{Ru(CO)(\mu\text{-}SPh)(\eta\text{-}C_5H_5)\}_2]$ was completely repressed and the chief product was $[Ru(CO)_2(SPh)(\eta\text{-}C_5H_5)]$. The complex $[Ru_2(CO)_2(\mu\text{-}SBu^t)(\mu\text{-}S_2Bu^t)(\eta\text{-}C_5H_5)_2]$ was then treated with S_2Ph_2 under u.v. irradiation in an effort to achieve SR group exchange, but the result was totally unexpected, a 45% yield of $[Ru(CO)\{SC_6H_4(SPh)\text{-}o\}(\eta\text{-}C_5H_5)]$ (12; M = Ru)[8] whose chemistry will be described in detail in Part 5 of this series.

The iron analogue (12; M = Fe) has been subsequently prepared[8] and found to have properties identical with those of a complex thought[4] to be a third isomer of $[\{Fe(CO)(\mu\text{-}SPh)(\eta\text{-}C_5H_5)\}_2]$. Each of $[\{M(CO)(\mu\text{-}SPh)(\eta\text{-}C_5H_5)\}_2]$ (M = Fe or Ru) is thus now shown to exist as a single *cis* and a single *trans* isomer.



(12)

EXPERIMENTAL

Varian Associates HA100 and JEOL PS100 instruments were employed in recording n.m.r. spectra. Irradiations were performed on reactants in Pyrex glassware with a 250-W mercury-vapour lamp. Commercially obtained disulphides and diphenyl diselenide were used without further purification. Preparation of $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2]$ was as described in the literature.[18]

Reactions of $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2]$ *with* E_2R_2.—Toluene (100 cm^3) solutions of $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (0.44 g, 1.0 mmol) with a 5—15 fold excess of E_2R_2 were subjected to u.v. irradiation for 17 h at both room temperature and at reflux. Solvent was then evaporated at reduced pressure and the orange-brown residue introduced onto a 30 × 2 cm alumina column. Elution with various dichloromethane–hexane solvent mixtures provided products as laid out in Table 3, given in their order of elution and with their yield. Complexes were purified by crystallisation from dichloromethane–hexane and the volatile $[Ru(CO)_2(SMe)(\eta\text{-}C_5H_5)]$ by additional sublimation (40 °C, 10^{-1} Torr) * onto a water-cooled probe.

Reaction of $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2]$ *with* S_2Ph_2–S.—A mixture of $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (0.44 g, 1.0 mmol), S_2Ph_2 (1.5 g, 7.0 mmol), and sulphur (0.5 g, 0.016 g atom) in toluene (100 cm^3) was irradiated for 17 h. Evaporation of solvent and chromatography then yielded with dichloromethane–hexane (1 : 3) a trace amount of $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2]$, with (2 : 3) yellow $[Ru(CO)_2(SPh)(\eta\text{-}C_5H_5)]$ (0.2 g, 30%), and with neat dichloromethane a small amount of an orange powder, m.p. 118—119 °C, ν(CO) at 1 957s, br and 1 935vs, br cm^{-1} (in CH_2Cl_2), which was not identified.

'Dimerisation' of $[Ru(CO)_2(ER)(\eta\text{-}C_5H_5)]$.—Toluene (50 cm^3) solutions of $[Ru(CO)_2(SR)(\eta\text{-}C_5H_5)]$ were either heated under reflux, or irradiated, for 17 h. Treatment of the solution obtained as above, with chromatography on a 15 × 2 cm alumina column, gave the products in Table 4. Heating of a similar quantity of $[Ru(CO)_2(SePh)(\eta\text{-}C_5H_5)]$ in heptane gave *cis*-$[\{Ru(CO)(\mu\text{-}SePh)(\eta\text{-}C_5H_5)\}_2]$ exclusively

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* Throughout this paper: 1 Torr = (101. 325/760) Nm^{-2}.

[16] R. M. Lynden-Bell, in *Progr. N.M.R. Spectroscopy*, 1967, **2**, 181.

[17] R. J. Cross, T. H. Green, and R. Keat, *J.C.S. Dalton*, 1976, 1150.

[18] A. P. Humphries and S. A. R. Knox, *J.C.S. Dalton*, 1975, 1710.

after 5 min, which was converted into *trans*-[{Ru(CO)(μ-SePh)(η-C_5H_5)}$_2$] on continued heating overnight (*ca.* 15 h). Products were identified by i.r. spectroscopy.

Isomerisation of [{Ru(CO)(μ-ER)(η-C_5H_5)}$_2$].—Separate samples (20 mg) of the *cis* and *trans* isomer of [{Ru(CO)(μ-C_5H_5)}$_2$] (ER = SMe, SCH_2Ph, Bu^t/SBu^t, SPh, or SePh) in toluene (50 cm^3) solution were either heated or irradiated for 17 h and the products (described in the text) identified by i.r. spectroscopy.

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