Thermolysis of Some Carbamatotetracarbonyl- and Carbamatopentacarbonyl-rhenium(I) Complexes in the Solid State and in Solution

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A series of carbamatocarbonylrhenium(I) complexes, [Re(CO)$_4$(XYCNMe$_2$)] (XY = SS, SSe, or SeSe) and [Re(CO)$_5${X(O)CNMe$_2$}] (X = S or Se), has been prepared. Thermolysis of these complexes in the solid state under flowing nitrogen or carbon monoxide affords binuclear complexes doubly bridged by sulphur or selenium, [{Re(CO)$_3$(XYCNMe$_2$)}$_2$], [{Re(CO)$_4$[X(O)CNMe$_2$]}$_2$], and [{Re(CO)$_3$[X(O)CNMe$_2$]}$_2$], as confirmed by i.r. and mass spectroscopy. Infrared spectra also reveal that [{Re(CO)$_3$[S(O)CNMe$_2$]}$_2$] adopts a *syn* configuration while the other dirhenium complexes assume *anti* forms. The complex [Re(CO)$_5${X(O)CNMe$_2$}] also undergoes thermolysis in cyclohexane to yield the same product as in the solid state; a mechanism is presented on the basis of time-dependent i.r. spectra.

IN a previous paper [1] we reported that (*i*) the solid-state thermolysis of [Mn(CO)$_4$(XYCNMe$_2$)] (XY = SS, SSe, or SeSe) under dry nitrogen evolved one molecule of carbon monoxide to give dimanganese complexes, [{Mn(CO)$_3$(XYCNMe$_2$)}$_2$], quantitatively, which involve bridging sulphur and/or selenium atoms, and (*ii*) [Mn(CO)$_5${X(O)CNMe$_2$}] (X = S or Se) with unidentate thio- or seleno-carbamate co-ordinated through the sulphur or selenium underwent thermolysis to yield similar dimanganese complexes, [{Mn(CO)$_3$[X(O)CNMe$_2$]}$_2$].

As an extension of this work, we attempted to examine the thermolysis of a series of carbamatocarbonylrhenium(I) complexes on a differential scanning calorimeter. Of these complexes, only [Re(CO)$_4$(S$_2$CNMe$_2$)] had been prepared previously by the reaction of [{Re(CO)$_3$(S$_2$CNMe$_2$)}$_2$] with carbon monoxide in benzene.[2] This paper reports the solid-state thermolysis of [Re(CO)$_4$(XYCNMe$_2$)] (XY = SS, SSe, or SeSe) and [Re(CO)$_5${X(O)CNMe$_2$}] (X = S or Se) under flowing nitrogen and carbon monoxide, yielding dirhenium(I) complexes, [{Re(CO)$_3$(XYCNMe$_2$)}$_2$] and [{Re(CO)$_n$[X(O)CNMe$_2$]}$_2$] (n = 3 or 4). The mechanism of dimerization of [Re(CO)$_5${X(O)CNMe$_2$}] (X = S or Se) in cyclohexane is also described on the basis of time-dependent i.r. spectra.

EXPERIMENTAL

Starting Materials and General Procedure.—The compounds SnMe$_2$Cl(SSeCNMe$_2$) [3] and SnMe$_2$(Se$_2$CNMe$_2$)$_2$ [4] were prepared as described previously. Dimethylammonium dimethyldithiocarbamate,[5] dimethylmonothiocarbamate,[6] dimethylmonoselenocarbamate,[7] and [Re(CO)$_5$Br] [8] were obtained by the literature methods. Preparation of monorhenium(I) complexes was carried out under dry nitrogen.

Tetracarbonyl(dimethyldithiocarbamato)rhenium(I), [Re(CO)$_4$(S$_2$CNMe$_2$)].—A suspension of [Re(CO)$_5$Br] (0.74 mmol) in a benzene (30 cm^3) solution of [NMe$_2$H$_2$][S$_2$CNMe$_2$] (0.74 mmol) was stirred for 1 h at room temperature, followed by filtration to remove [NMe$_2$H$_2$]Br. The filtrate was shaken three times with water (10 cm^3) to remove [NMe$_2$H$_2$]Br dissolved in benzene. The benzene layer was separated and dried with Mg[SO$_4$]. The Mg[SO$_4$] was filtered off, the filtrate was evaporated to dryness under reduced pressure (*ca*. 10 mmHg) † at room temperature, and the product was sublimed (60 °C, 10^{-3} mmHg) in 60% yield.

Dimethylselenothiocarbamato- and Dimethyldiselenocarbamato-tetracarbonylrhenium(I), [Re(CO)$_4$L] (L = SSeCNMe$_2$ *or* Se$_2$CNMe$_2$).—A suspension of [Re(CO)$_5$Br] (0.74 mmol) in benzene (25 cm^3) containing SnMe$_2$Cl(SSeCNMe$_2$) (0.74 mmol) was stirred for 2 h at 50 °C. The solution was cooled to room temperature, and SnBrMe$_2$Cl formed in solution was extracted three times with water (10 cm^3). The benzene layer was separated and evaporated to dryness under reduced pressure to give [Re(CO)$_4$(SSeCNMe$_2$)], which was sublimed (60 °C, 10^{-3} mmHg) in 60% yield. The [Re(CO)$_4$(Se$_2$CNMe$_2$)] was similarly prepared by reaction of [Re(CO)$_5$Br] (0.74 mmol) with SnMe$_2$(Se$_2$CNMe$_2$)$_2$ (0.74 mmol) in benzene and purified by sublimation (60 °C, 10^{-1} mmHg) in 64% yield.

Dimethylmonothiocarbamato- and Dimethylmonoselenocarbamato-pentacarbonylrhenium(I), [Re(CO)$_5$L′] [L′ = S(O)CNMe$_2$ *or* Se(O)CNMe$_2$].—These complexes were synthesized by reaction of [Re(CO)$_5$Br] (0.74 mmol) with [NMe$_2$H$_2$][L′] (0.74 mmol) in benzene similarly to [Re(CO)$_4$(S$_2$CNMe$_2$)], followed by sublimation (40 °C, 10^{-1} mmHg) in 60 [L′ = S(O)CNMe$_2$] or 50% yield [L′ = Se(O)CNMe$_2$].

Thermolysis.—Powdered [Re(CO)$_4$L] (*ca*. 10 mg; L = S$_2$CNMe$_2$, SSeCNMe$_2$ *or* Se$_2$CNMe$_2$) was heated to 160 °C in a Shimazu SC-20 differential scanning calorimeter (d.s.c.) at a scanning rate of 2.5 °C min^{-1} under flowing nitrogen (30 cm^3 min^{-1}). After cooling the d.s.c. cell the complexes [{Re(CO)$_3$L}$_2$], were obtained. Under the same conditions, [Re(CO)$_5$L′] heated to 170 [L′ = S(O)CNMe$_2$] or 190 °C [L′ = Se(O)CNMe$_2$] gave [{Re(CO)$_3$L′}$_2$].

On the other hand, heating [Re(CO)$_5$L′] to 130 °C in a d.s.c. cell with the same scanning rate under flowing carbon monoxide afforded [{Re(CO)$_4$L′}$_2$]. All the dirhenium complexes were obtained quantitatively. They were analytically pure without any purification (Table 1).

Physical Measurements.—Infrared spectra were recorded on a Hitachi–Perkin-Elmer 225 spectrophotometer with 1.0 and 0.5 mm KRS-5 cells. Mass spectra were obtained with a Hitachi RMU-6E spectrometer.

RESULTS AND DISCUSSION

Thermolysis of Mononuclear Complexes.—Figure 1 shows the thermogram of two representative complexes, [Re(CO)$_4$(S$_2$CNMe$_2$)] and [Re(CO)$_5${S(O)CNMe$_2$}] in the solid state. The S$_2$CNMe$_2$ complex exhibited only one endothermic peak at *ca*. 150 °C under flowing nitrogen and gave [{Re(CO)$_3$(S$_2$CNMe$_2$)}$_2$], confirmed by the

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† Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

elemental analysis and mass spectrum (M^+ at m/e 781. Calc. 781). The thermolysis of $[Re(CO)_4L]$ (L = $SSeCNMe_2$ or Se_2CNMe_2) also showed only a peak at *ca.*

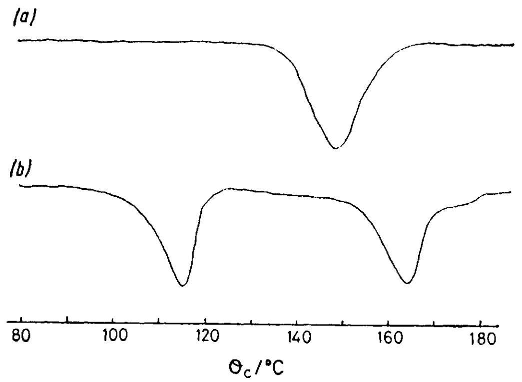

FIGURE 1 Thermogram of (*a*) $[Re(CO)_4(S_2CNMe_2)]$ under nitrogen and (*b*) $[Re(CO)_5\{S(O)CNMe_2\}]$ under carbon monoxide

120 and 160 °C and afforded $[\{Re(CO)_3L\}_2]$ respectively.

On the other hand, two endothermic peaks were observed in the thermogram of $[Re(CO)_5\{S(O)CNMe_2\}]$ not only under carbon monoxide but also under dry nitrogen at *ca.* 115 and 150 °C (Figure 1). The product obtained at the temperature of the first peak under carbon monoxide was identified as $[\{Re(CO)_4[S(O)CNMe_2]\}_2]$ on the basis of the elemental analysis and mass spectra (M^+ at m/e 805. Calc. 805). However, thermolysis at the temperature of the second peak under carbon monoxide afforded a mixture of $[\{Re(CO)_4L'\}_2]$ and $[\{Re(CO)_3L'\}_2]$ [L' = $S(O)CNMe_2$]. The same mixture was obtained when pure $[\{Re(CO)_3[S(O)CNMe_2]\}_2]$ was allowed to stand in a d.s.c. cell at *ca.* 150 °C under a stream of carbon monoxide.

The thermolysis of $[Re(CO)_5\{S(O)CNMe_2\}]$ at the first endothermic peak under nitrogen also yielded a mixture of $[\{Re(CO)_4L'\}_2]$ and $[\{Re(CO)_3L'\}_2]$ [L' = $S(O)CNMe_2$] (*ca.* 4 : 1), as confirmed by i.r. spectra in Nujol mulls. The formation of the mixture may correspond to the appearance of a peak accompanied by a shoulder (Figure 1). The formation ratio of these binuclear complexes was not changed on prolonged heating at a fixed temperature near that of the first peak. In addition, $[\{Re(CO)_4[S(O)CNMe_2]\}_2]$ obtained under carbon monoxide exhibited no endothermic peak at all up to 130 °C under nitrogen. This result confirms that the formation of $[\{Re(CO)_3[S(O)CNMe_2]\}_2]$ under nitrogen at such low temperatures may not be attributed to a stepwise pathway *via* $[\{Re(CO)_4[S(O)CNMe_2]\}_2]$, although the mechanism has not been elucidated in the present study. The product obtained at the second endothermic peak under nitrogen was identified as $[\{Re(CO)_3[S(O)CNMe_2]\}_2]$ on the basis of elemental analysis and mass spectra (M^+ at m/e 749. Calc. 749).

The $[Re(CO)_5\{Se(O)CNMe_2\}]$ complex showed a similar thermolytic behaviour to the $S(O)CNMe_2$ analogue not only under carbon monoxide but also under nitrogen, except that it underwent thermolysis at somewhat higher temperatures. Table 2 summarizes the thermochemical data for the complexes.

Configuration of the Mononuclear Complexes.—Infrared spectra of $[Re(CO)_4L]$ (L = S_2CNMe_2, $SSeCNMe_2$, or Se_2CNMe_2) showed a strong band due to the carbamate C⋯N bond stretch at *ca.* 1 530 cm^{-1}, while $[Re(CO)_5L']$ exhibited the ν(C=O) band at 1 605 cm^{-1} for L' = $S(O)CNMe_2$ and 1 621 cm^{-1} for L' = $Se(O)CNMe_2$, as shown in Table 3. In addition, $[Re(CO)_4L]$ and $[Re(CO)_5L']$ displayed four and five * absorptions in the ν(C≡O) region respectively (Table 3). These i.r. patterns are very similar to those of $[Mn(CO)_4L]$ or $[Mn(CO)_5L']$ reported previously.[1] Thus, the same discussion as for the manganese(I) complexes leads us to the conclusion that both $[Re(CO)_4L]$ and $[Re(CO)_5L']$ adopt octahedral geometries, in which the ligands L co-ordinate to Re in a bidentate manner, while L' act as unidentate ligands with co-ordination of sulphur or selenium.

TABLE 1

Elemental analysis and properties of the complexes

Complex	Colour	M.p. (θ_c/°C)	Found (%) [b] C	H	N
$[Re(CO)_4(S_2CNMe_2)]$	White	120	20.2 (20.1)	1.50 (1.45)	3.25 (3.35)
$[Re(CO)_4(SSeCNMe_2)]$	White	120	17.8 (18.05)	1.30 (1.30)	2.95 (3.00)
$[Re(CO)_4(Se_2CNMe_2)]$	White	135	16.3 (16.4)	1.40 (1.20)	2.85 (2.75)
$[Re(CO)_5\{S(O)CNMe_2\}]$	White	98	22.3 (22.35)	1.45 (1.40)	3.45 (3.25)
$[Re(CO)_5\{Se(O)CNMe_2\}]$	White	103	20.0 (20.15)	1.30 (1.25)	2.85 (2.95)
$[\{Re(CO)_4[S(O)CNMe_2]\}_2]$	Pale yellow	131	20.8 (20.9)	1.45 (1.50)	3.60 (3.50)
$[\{Re(CO)_4[Se(O)CNMe_2]\}_2]$	Pale yellow	175	18.75 (18.7)	1.35 (1.35)	3.15 (3.10)
$[\{Re(CO)_3(S_2CNMe_2)\}_2]$	Pale green	290	18.65 (18.45)	1.60 (1.55)	3.60 (3.60)
$[\{Re(CO)_3(SSeCNMe_2)\}_2]$	Pale green	300	16.4 (16.5)	1.45 (1.40)	3.30 (3.20)
$[\{Re(CO)_3(Se_2CNMe_2)\}_2]$	Pale green	300	15.0 (14.9)	1.40 (1.25)	2.95 (2.90)
$[\{Re(CO)_3[S(O)CNMe_2]\}_2]$	Pale yellow	250	19.3 (19.25)	1.50 (1.60)	3.80 (3.75)
$[\{Re(CO)_3[Se(O)CNMe_2]\}_2]$	Pale yellow	250	17.1 (17.1)	1.40 (1.45)	3.30 (3.35)

[a] With decomposition. [b] Calculated values are given in parentheses.

Configuration of $[\{Re(CO)_3L\}_2]$ *and* $[\{Re(CO)_3L'\}_2]$ [L = S_2CNMe_2, $SSeCNMe_2$, *or* Se_2CNMe_2; L' = $S(O)CNMe_2$ *or* $Se(O)CNMe_2$].—There are two possible configurations, (1) (*anti*) and (2) (*syn*), for $[\{Re(CO)_3L\}_2]$ and $[\{Re(CO)_3L'\}_2]$. These configurations belong to the point groups C_i and C_s, which predict the appearance of

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* The $[Re(CO)_5L']$ complexes [L' = $S(O)CNMe_2$ or $Se(O)CNMe_2$] are expected to exhibit three i.r.-active ν(C≡O) bands, $2A_1 + E$, under the local symmetry of C_{4v}. The appearance of five bands may be due to splitting of the E fundamental and the occurrence of a B_1 mode as i.r. active, because of the lowering of symmetry by the co-ordination of L'. Similar splitting was reported in the case of $[Mn(CO)_5L']$ (see ref. 1).

TABLE 2

Thermochemical data

	T_i [a] (°C)	T_p [b] (°C)	T_f [c] (°C)	Flowing gas [d]	ΔH/[e] kJ mol^{-1}	Back reaction [f]
$[Re(CO)_4(S_2CNMe_2)] \longrightarrow \frac{1}{2}[\{Re(CO)_3(S_2CNMe_2)\}_2]$	132	148	163	N_2	47.72 ± 0.33	Yes
$[Re(CO)_4(SSeCNMe_2)] \longrightarrow \frac{1}{2}[\{Re(CO)_3(SSeCNMe_2)\}_2]$	106	117	124	N_2	36.98 ± 0.45	No
$[Re(CO)_4(Se_2CNMe_2)] \longrightarrow \frac{1}{2}[\{Re(CO)_3(Se_2CNMe_2)\}_2]$	143	157	164	N_2	27.34 ± 0.75	No
$[Re(CO)_5\{S(O)CNMe_2\}] \longrightarrow \frac{1}{2}[\{Re(CO)_4[S(O)CNMe_2]\}_2]$	90	115	120	CO	31.00 ± 1.81	No
$[\{Re(CO)_4[S(O)CNMe_2]\}_2] \longrightarrow [\{Re(CO)_3[S(O)CNMe_2]\}_2]$	150	161	167	N_2	33.55 ± 0.90	Yes
$[Re(CO)_5\{Se(O)CNMe_2\}] \longrightarrow \frac{1}{2}[\{Re(CO)_4[Se(O)CNMe_2]\}_2]$	110	127	132	CO	27.57 ± 1.71	No
$[\{Re(CO)_4[Se(O)CNMe_2]\}_2] \longrightarrow [\{Re(CO)_3[Se(O)CNMe_2]\}_2]$	164	179	189	N_2	36.95 ± 0.50	Yes

[a] Initial temperature. [b] The temperature at which the reaction rate was largest. [c] Final temperature. [d] 30 cm^3 min^{-1}. [e] Value per rhenium atom. [f] In cyclohexane under atmospheric pressure of carbon monoxide.

TABLE 3

Infrared bands (cm^{-1}) of the complexes

Complex	Solvent	$\nu(C\equiv O)$						$\nu(C{=}O)$ or $\nu(C\cdots N)$
$[Re(CO)_4(S_2CNMe_2)]$	*a*	2 098	1 996	1 978	1 935			1 530
$[Re(CO)_4(SSeCNMe_2)]$	*a*	2 098	1 998	1 980	1 937			1 535
$[Re(CO)_4(Se_2CNMe_2)]$	*a*	2 095	1 996	1 976	1 935			1 530
$[Re(CO)_5\{S(O)CNMe_2\}]$	*b*	2 143	2 083	2 039	20 32	1 985		1 605
$[Re(CO)_5\{Se(O)CNMe_2\}]$	*b*	2 134	2 069	2 025	2 021	1 982		1 621
anti-$[\{Re(CO)_3(S_2CNMe_2)\}_2]$	*a*	2 035	2 017	1 913				1 543
anti-$[\{Re(CO)_3(SSeCNMe_2)\}_2]$	*a*	2 031	2 015	1 910				1 548
anti-$[\{Re(CO)_3(Se_2CNMe_2)\}_2]$	*a*	2 028	2 013	1 910				1 542
syn-$[\{Re(CO)_3[S(O)CNMe_2]\}_2]$ [c]	*b*	2 043	2 027	1 938	1 930	19 20	1 914	1 586
anti-$[\{Re(CO)_3[Se(O)CNMe_2]\}_2]$	*b*	2 024	1 929	1 911				1 583
anti-$[\{Re(CO)_4[S(O)CNMe_2]\}_2]$ [d]	*b*	2 104	2 030	1 993	1 953			1 661
anti-$[\{Re(CO)_4[Se(O)CNMe_2]\}_2]$	*b*	2 092	2 015	1 992	1 952			1 665

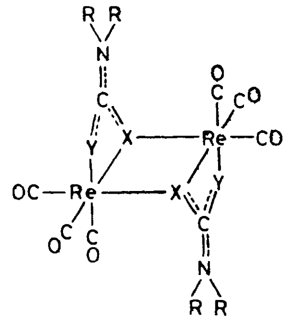
[a] Dichloromethane. [b] Cyclohexane. [c] $\nu(C\equiv O)$ at 2 041, 2 026, and 1 992 cm^{-1} and $\nu(C{=}O)$ at 1 597 cm^{-1} in dichloromethane. [d] For *syn*-$[\{Re(CO)_4[S(O)CNMe_2]\}_2]$ in cyclohexane: 2 100, 2 073, 2 033, 2 025, 2 000, 1 986, and 1 945 cm^{-1} for $\nu(C\equiv O)$ and 1 665 cm^{-1} for $\nu(C{=}O)$.

TABLE 4

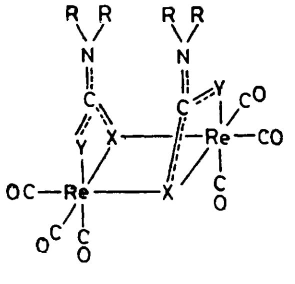
Mass-spectral data for $[\{Re(CO)_4[X(O)CNMe_2]\}_2]$

X = S			X = Se		
m/*e*	Relative intensity	Assignment	*m*/*e*	Relative intensity	Assignment
290	67	$[Re\{S(O)CNMe_2\}]^+$			
404	43	$[Re_2S]^+$	451	7	$[Re_2Se]^+$
			473	100	$[Re\{Se(O)CNMe\}\{Se(O)CNMe_2\}]^+$
			488	75	$[Re\{Se(O)CNMe_2\}_2]^+$
581	39	$[M - 8CO]^+$	675	9	$[M - 8CO]^+$
609	58	$[M - 7CO]^+$	703	44	$[M - 7CO]^+$
637	19	$[M - 6CO]^+$	731	24	$[M - 6CO]^+$
665	74	$[M - 5CO]^+$	759	58	$[M - 5CO]^+$
693	100	$[M - 4CO]^+$	787	72	$[M - 4CO]^+$
721	29	$[M - 3CO]^+$	815	29	$[M - 3CO]^+$
749	83	$[M - 2CO]^+$	843	88	$[M - 2CO]^+$
777	6	$[M - CO]^+$	871	5	$[M - CO]^+$
805	7	$[\{Re(CO)_4[S(O)CNMe_2]\}_2]^+$ ($[M]^+$)	899	9	$[\{Re(CO)_4[Se(O)CNMe_2]\}_2]^+$ ($[M]^+$)

three and six i.r.-active $\nu(C\equiv O)$ bands, respectively. The spectrum of $[\{Re(CO)_3[Se(O)CNMe_2]\}_2]$ in cyclohexane showed three $\nu(C\equiv O)$ fundamentals (Table 2), indicating configuration (1). The same geometry is suggested also for $[\{Re(CO)_3L\}_2]$ (L = S_2CNMe_2, $SSeCNMe_2$, or Se_2CNMe_2) on the basis of the appearance of three $\nu(C\equiv O)$ bands in the i.r. spectra in dichloromethane (Table 3), although the limited solubilities prevented the measurement of spectra in cyclohexane.



(1) (*anti*)



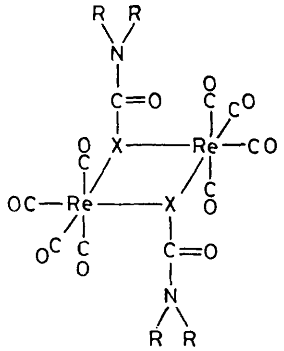
(2) (*syn*)

XY = SS, SSe, SeSe, SO, or SeO

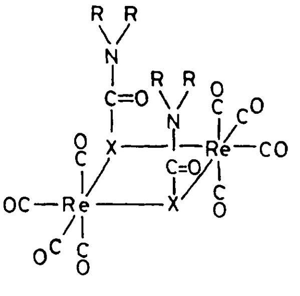
The spectrum of $[\{Re(CO)_3[S(O)CNMe_2]\}_2]$ in dichloromethane also showed three $\nu(C\equiv O)$ bands (see footnote *b* in Table 3), of which that at lowest frequency was very broad and gradually split when increasing amounts of cyclohexane were added to the dichloromethane solution. Finally, this complex in cyclohexane exhibited six $\nu(C\equiv O)$ bands (Table 3). Such spectral behaviour in solution was never observed for the corresponding $Se(O)CNMe_2$ complex. Thus, $[\{Re(CO)_3[S(O)CNMe_2]\}_2]$ in cyclohexane is suggested to assume configuration (2). It should be mentioned that the two *syn* and *anti* isomers of this complex may not coexist in any mixtures of dichloromethane and cyclohexane, since the $\nu(C{=}O)$ band at 1 597 cm^{-1} in dichloromethane gradually moved toward 1 586 cm^{-1} (the value in cyclohexane) with increasing amounts of cyclohexane, and two ν(C=O) bands have not been observed separately. Thus, $[\{Re(CO)_3[S(O)CNMe_2]\}_2]$ may still exist as the *syn* form in dichloromethane, and the occurrence of only three ν(C≡O) bands in this solvent is possibly due to solvent effects.

Configuration of $[\{Re(CO)_4L'\}_2]$ [L' = $S(O)CNMe_2$ *or* $Se(O)CNMe_2$].—Mass-spectral data for $[\{Re(CO)_4L'\}_2]$ are summarized in Table 4, which shows the occurrence of the $[Re_2S]^+$ or $[Re_2Se]^+$ fragments, but no $[Re_2O]^+$. This result suggests that the complexes involve bridging sulphur or selenium. This is supported by the i.r. spectra, which showed the ν(C=O) band at 1 661 [L' = $S(O)CNMe_2$] or 1 665 cm^{-1} [L' = $Se(O)CNMe_2$]. These bands are very close to that of $[\{Rh(CO)_2[S(O)CNMe_2]\}_2]$ (1 665 cm^{-1}) which has been reported to involve two bridging sulphurs and two terminal carbonyl groups.[9]

There are two possible configurations for $[\{Re(CO)_4L'\}_2]$, (3) (*anti*, C_{2h} symmetry) and (4) (*syn*, C_2 symmetry), which predict four and seven i.r.-active ν(C≡O) fundamentals, respectively. The spectra of $[\{Re(CO)_4L'\}_2]$ obtained by thermolysis showed four bands in cyclohexane (Table 3), indicating configuration (3). This is in contrast to $[\{Mn(CO)_4[Se(O)CNMe_2]\}_2]$ which adopts the *syn* configuration in cyclohexane.[10]



(3) *(anti)*



(4) *(syn)*

X = S or Se

Mechanism of Thermolysis in Solution.—The configurational assignments described above reveal that the solid-state thermolysis of *anti*-$[\{Re(CO)_4[Se(O)CNMe_2]\}_2]$ gives *anti*-$[\{Re(CO)_3[Se(O)CNMe_2]\}_2]$ with retention of configuration with respect to the orientation of the two $Se(O)CNMe_2$ ligands, while the corresponding $S(O)CNMe_2$ complex undergoes thermolysis with inversion of configuration to afford *syn*-$[\{Re(CO)_3[S(O)CNMe_2]\}_2]$.

The elimination of carbon monoxide also takes place in solution as confirmed by time-dependent i.r. spectra of *anti*-$[\{Re(CO)_4L'\}_2]$ [L' = $S(O)CNMe_2$ or $Se(O)CNMe_2$]. Figure 2 shows the spectra in the ν(C=O) region for the $S(O)CNMe_2$ complex in cyclohexane under dry nitrogen at 55 °C. Immediately after preparing the solution the complex exhibits a strong band at 1 661 cm^{-1}, which decreases in intensity with time. After several minutes a new band begins to appear at 1 550 cm^{-1} and reaches maximum intensity after *ca.* 1.4 h, followed by a gradual decrease in intensity and the occurrence of a new band at 1 586 cm^{-1}, which remains until the end of thermolysis. Finally, the solution exhibited six ν(C≡O) absorptions, indicating the formation of *syn*-$[\{Re(CO)_3[S(O)CNMe_2]\}_2]$ with ν(C=O) at 1 586 cm^{-1}. The transient band at 1 550 cm^{-1} is reasonably assigned to the bidentate $S(O)CNMe_2$ ligand[11] of monomeric $[Re(CO)_4\{S(O)CNMe_2\}]$. It is therefore suggested that *anti*-$[\{Re(CO)_4[S(O)CNMe_2]\}_2]$ first dissociates into two monomers in cyclohexane, followed by evolution of carbon monoxide and dimerization to *syn*-$[\{Re(CO)_3[S(O)CNMe_2]\}_2]$.

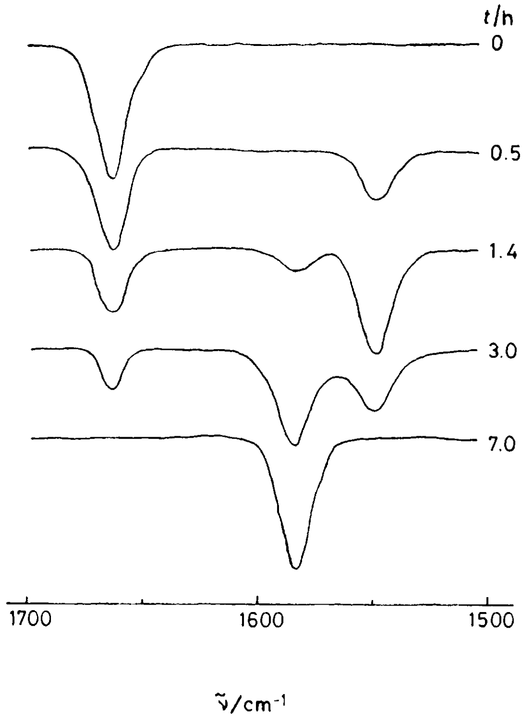


FIGURE 2 Infrared spectra [ν(C=O)] of $[\{Re(CO)_4[S(O)CNMe_2]\}_2]$ in cyclohexane at 55 °C

On the other hand, no ν(C=O) band assignable to monomeric $[Re(CO)_4\{Se(O)CNMe_2\}]$ has been found in the time-dependent i.r. spectra of *anti*-$[\{Re(CO)_4[Se(O)CNMe_2]\}_2]$ in cyclohexane; the band at 1 583 cm^{-1} due to *anti*-$[\{Re(CO)_3[Se(O)CNMe_2]\}_2]$ gradually increased in intensity with time at the expense of that at 1 665 cm^{-1}. This result, together with the retention of configuration, strongly suggests that the release of carbon monoxide from *anti*-$[\{Re(CO)_4[Se(O)CNMe_2]\}_2]$ is accompanied by intramolecular substitution of the $Se(O)CNMe_2$ oxygen for an axial CO molecule.

We also attempted the reaction of $[\{Re(CO)_3L'\}_2]$ [L' = $S(O)CNMe_2$ (*syn*) or $Se(O)CNMe_2$ (*anti*)] with carbon monoxide under atmospheric pressure (Table 2). A cyclohexane solution of the $Se(O)CNMe_2$ complex reversibly absorbed carbon monoxide bubbled into the solution (for a few hours at room temperature) to give *anti*-$[\{Re(CO)_4[Se(O)CNMe_2]\}_2]$ quantitatively

Similarly, the $S(O)CNMe_2$ complex in cyclohexane absorbed carbon monoxide (6 h, at 40 °C) to afford *syn*-$[\{Re(CO)_4[S(O)CNMe_2]\}_2]$ as confirmed by the occurrence of seven ν(C≡O) bands (Table **3**, footnote *c*) in the i.r. spectrum.

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