Halogenotricarbonylrhenium(I) Complexes of 2,6-Bis(thioalkyl)- and -(thioaryl)-pyridines, their Syntheses and Solution Stereodynamics

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Reactions of pentacarbonylhalogenorhenium(I) with 2,6-bis(*p*-tolylthiomethyl)pyridine (L^1) or 2,6-bis(methylthiomethyl)pyridine (L^2) afforded complexes of type *fac*-[ReX(CO)$_3$L] (X = Cl, Br or I; L = L^1 or L^2). These potentially tridentate ligands, L^1 and L^2, are here acting as bidentate N/S species forming five-membered ring chelate complexes. In an NMR study of both series of complexes, pyramidal inversion of the co-ordinated sulfur atoms was observed together with an intramolecular fluxional process which exchanges co-ordinated and unco-ordinated thioalkyl or thioaryl groups. The two processes have similar activation energies but were separately measurable in certain cases. Two possible mechanisms for the novel intramolecular exchange process are discussed.

Recent NMR studies by us have been concerned with the solution stereodynamics of transition-metal complexes of a range of hybrid sulfur/phosphorus ligands based on triphenylphosphine derivatives. The ligands in question were [*o*-(methylthio)phenyl]diphenylphosphine, bis[*o*-(methylthio)phenyl]phenylphosphine and tris[*o*-(methylthio)phenyl]phosphine. All three potentially tridentate ligands act as bidentate species towards transition metals forming five-membered chelate ring complexes. The $PPh_2(C_6H_4SMe\text{-}o)$ complexes of trimethylplatinum(IV) halides[1] and halogenotricarbonylrhenium(I)[2] exhibit pyramidal sulfur inversion of the co-ordinated S atom. Complexes of the last two ligands with halogenotricarbonylrhenium(I)[2] and palladium(II) or platinum(II) dihalides[3] contain one or two unco-ordinated pendant MeS groups. The PdX_2 and PtX_2, but not the $ReX(CO)_3$, complexes were shown to undergo intramolecular exchange of the pendant and the co-ordinated MeS groups at rates comparable to those of the pyramidal sulfur-inversion process which also occurs.

The present work was initiated in order to examine whether this novel type of fluxional exchange process is associated with other types of hybrid ligands. We accordingly chose the hybrid nitrogen/sulfur ligands 2,6-bis(*p*-tolylthiomethyl)pyridine (L^1) and 2,6-bis(methylthiomethyl)pyridine (L^2) and treated them with [ReX(CO)$_5$]. Octahedral complexes of type *fac*-[ReX(CO)$_3$L] (L = L^1 or L^2; X = Cl, Br or I) were formed and their static and dynamic structures have now been examined by solution NMR spectroscopy.

Experimental

Materials.—The pentacarbonylhalogenorhenium(I) complexes were prepared by previous methods.[4,5] The ligand L^1 was synthesised by a literature method,[6] whereas L^2 was prepared by a new route described below.

2,6-*Bis(methylthiomethyl)pyridine*. The following reactants were combined in benzene–water (1:1, 50 cm^3) solvent at 0 °C: sodium hydroxide (1.4 g, 0.035 mol), 2,6-bis(dibromomethyl)pyridine (4.0 g, 0.015 mol),[7] Adogen 464 (Aldrich) phase-transfer catalyst (eight drops), and MeSH (2 g, 0.042 mol). The mixture was stirred vigorously at 0 °C for 30 min, followed by stirring at ambient temperature for 3 d. The organic layer was separated and dried over magnesium sulfate. Concentration of the liquid *in vacuo* gave an oil which required no further purification. Yield 1.2 g (40%). ^{1}H NMR data ($CDCl_3$ solution): δ 7.64 (t, ^3J = 7.8, H^4 ring proton), 7.24 (d, ^3J = 7.8 Hz, $H^{3,5}$ ring protons), 3.78 (s, CH_2) and 2.06 (s, CH_3S). Mass spectrometry data: *m/z* 199 (M^+), 184 ($M - CH_3$), 153 ($M - S$) and 106 ($M - SCH_3$).

Synthesis of Complexes.—All six complexes were prepared by the same route, with only the reactant time varying (see Table 1). All manipulations were carried out under nitrogen, and freshly dried solvents were used in all reactions. The procedure for the complex [ReI(CO)$_3$L^1] is given below.

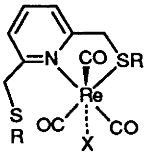
[2,6-*Bis*(p-*tolylthiomethyl*)*pyridine*]*tricarbonyliodorhenium*(I). The complex [ReI(CO)$_5$] (0.25 g, 0.41 mmol) and ligand L^1 (0.27 g, 0.78 mmol) were dissolved in tetrahydrofuran (thf) and heated under reflux for 80 h. After this period of time the IR spectrum of the reaction mixture showed new bands in the carbonyl stretching region, and the C≡O bands due to the starting material were absent. The solution was concentrated to dryness *in vacuo* and the white residue washed with hexane. Recrystallisation from dichloromethane and hexane gave the desired product. Yield 0.19 g (61%). Synthetic and analytical details for this and the other complexes are given in Table 1.

Physical Methods.—Infrared spectra of the complexes in thf solutions were recorded on a Perkin-Elmer model 881 spectrophotometer in the region 2200–1800 cm^{-1}, ^{1}H NMR spectra using a Bruker AM 250 FT spectrometer operating at 250.13 MHz. Chemical shifts are quoted relative to $SiMe_4$ as an internal standard. All NMR spectra were recorded as solutions in $CDCl_3$, CD_2Cl_2 or $CDCl_2CDCl_2$. Mass spectra were recorded on a Hitachi–Perkin-Elmer RMU-6 spectrometer operating in the electron-impact ionisation mode.

Elemental analyses were carried out by Butterworth Laboratories, Teddington, Middlesex. Melting points were recorded on a digital Gallenkamp apparatus and were uncorrected. The NMR bandshape analyses were performed using the authors' version of the original DNMR3 program of Kleier and Binsch.[8] Computer-simulated spectra were fitted visually with experimental spectra. Activation energies were obtained from least-squares fittings of standard Arrhenius and Eyring plots. The errors quoted for $\Delta G^\ddagger$ are as defined by Binsch and Kessler.[9]

Results

Moderate yields of the six complexes were obtained using the above methods (Table 1). Infrared spectroscopy proved to be a convenient means of monitoring the reactions. Three carbonyl stretching bands (2A′ + A″) are expected for a molecule possessing three CO groups in an idealised *fac* configuration.[10] For the present complexes all three bands were not always observed due to the broad nature of certain of them (Table 1).



	R	X
1	C_6H_4Me-*p*	Cl
2	C_6H_4Me-*p*	Br
3	C_6H_4Me-*p*	I
4	Me	Cl
5	Me	Br
6	Me	I

Infrared and NMR spectra (see below) provide evidence for the complexes possessing octahedral symmetry at the Re atom with the ligand acting in a N/S bidentate mode and forming a five-membered chelate ring. The three carbonyl groups are attached to Re in a facial arrangement.

Low-temperature NMR Studies.—$[ReX(CO)_3(L^1)]$ (X = Cl *or* Br). On cooling solutions of these complexes in CD_2Cl_2 to *ca.* −10 °C well resolved ^1H NMR spectra were obtained showing no evidence of any exchange process. The ^1H spectrum of $[ReCl(CO)_3L^1]$ **1** at 0 °C is illustrated (Fig. 1), showing the three principal regions of interest. The ligand methyl region, around δ 2.5, shows two pairs of signals of widely differing

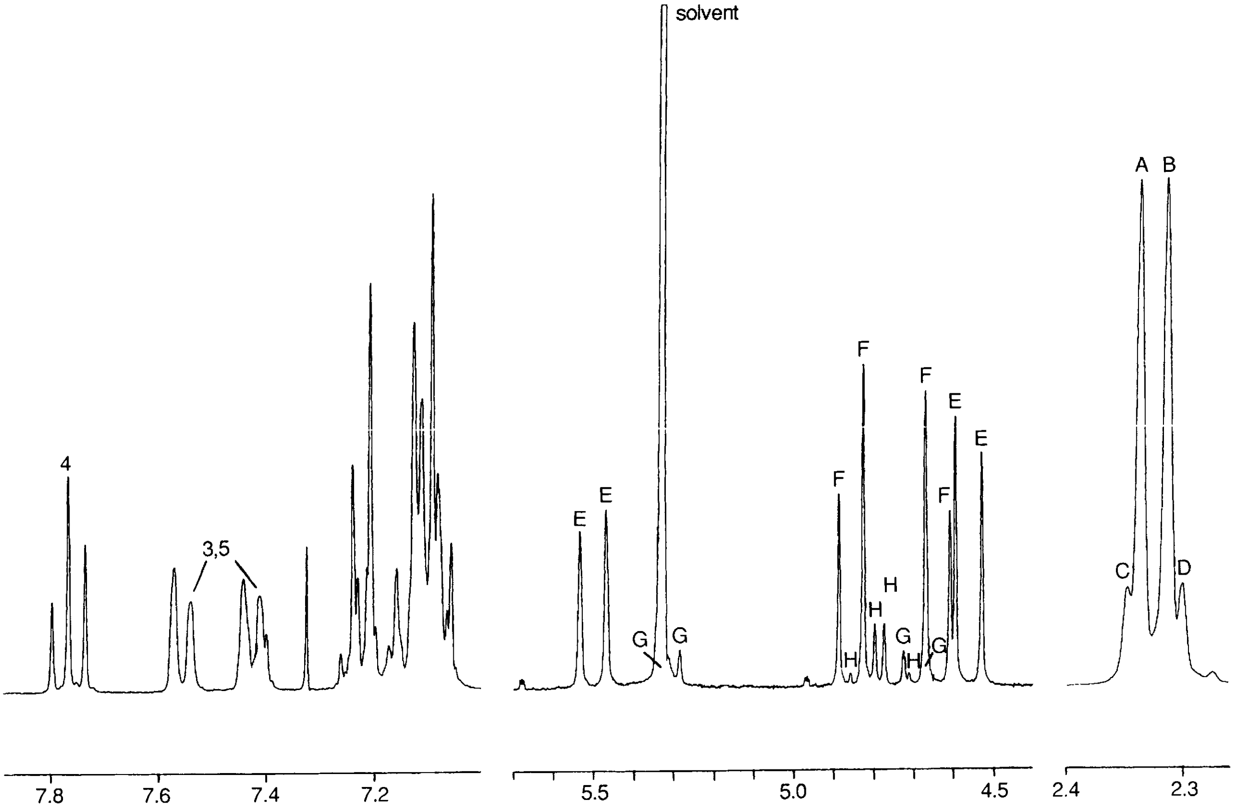


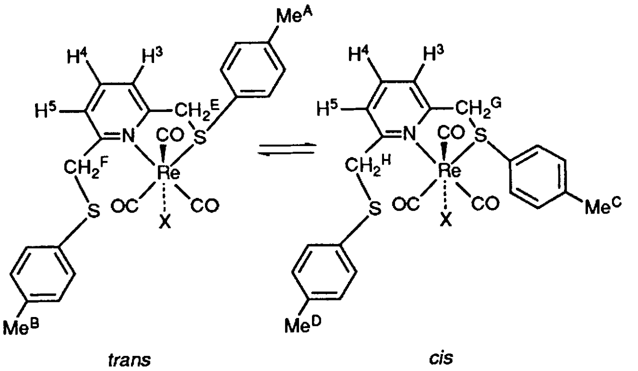
Fig. 1 The ^1H NMR spectrum of $[ReCl(CO)_3L^1]$ at 0 °C showing the three principal regions of interest. The labelling refers to Scheme 1

Table 1 Synthetic and analytical details of the complexes *fac*-$[ReX(CO)_3(L–L)]$ [X = Cl, Br or I; L–L = 2,6-bis(*p*-tolylthiomethyl)pyridine (L^1) or 2,6-bis(methylthiomethyl)pyridine (L^2)]

Complex	Reaction time/h	Yield[a] (%)	Melting temperature (°C)	$\tilde{\nu}(CO)$[b]/cm^{-1}	Analysis (%)[c]		
					C	H	N
1 $[ReCl(CO)_3L^1]$	1.5	42	169	2029vs, 1921s, 1900vs	43.9 (44.0)	3.25 (3.20)	2.15 (2.15)
2 $[ReBr(CO)_3L^1]$	12	47	180	2027s, 1899vs (vbr)[d]	41.1 (41.3)	3.25 (2.95)	2.00 (2.10)
3 $[ReI(CO)_3L^1]$	80	61	192	2028s, 1905vs (vbr)[d]	38.5 (38.5)	3.05 (2.75)	1.85 (1.90)
4 $[ReCl(CO)_3L^2]$	4	42	165	2028s, 1895vs (vbr)[d]	28.5 (28.7)	2.60 (2.45)	2.75 (2.70)
5 $[ReBr(CO)_3L^2]$	9	36	176	2029vs, 1926s, 1900vs	26.2 (26.7)	2.40 (2.20)	2.55 (2.60)
6 $[ReI(CO)_3L^2]$	114	29	169	2028vs, 1925s, 1902vs	24.2 (24.4)	2.20 (1.95)	2.35 (2.40)

[a] Quoted relative to $[ReX(CO)_5]$. [b] Recorded in thf solution; s = strong, v = very, br = broad. [c] Calculated values in parentheses. [d] Unresolved.

intensity. The two pairs of signals are attributed to the two possible invertomers of the complex, labelled *trans* and *cis* with respect to the relative orientation of the co-ordinated *p*-MeC_6H_4S group and the halogen (Scheme 1). The *cis* isomer, where these two groups are adjacent, is clearly disfavoured and thus the intense methyl signals are attributed to the *trans* isomer. Individual signal assignments were made on the basis that methyls Me^A and Me^C will be deshielded compared to Me^B and Me^D by the rhenium co-ordination shift. The population ratio of *trans*/*cis* was 81:19. For complex **2** (X = Br) this ratio was even larger in favour of the *trans* invertomer, but due to signal overlaps it could not be measured precisely. The methylene region of the spectrum of complex **1** consisted of four overlapping AB quartets, two of high and two of low intensity. The quartets labelled E and G (Fig. 1) with relatively large internal chemical shifts were attributed to the methylenes of the chelate ring since these nuclei, by virtue of their closeness to the site of inversion, will be most sensitive to the orientation of the *p*-MeC_6H_4S group. These large chemical shift differences reflect the considerable chemical shielding anisotropy of the aromatic ring. The aromatic region of the spectrum could not be fully assigned but the three non-equivalent hydrogens of the pyridine were identified without difficulty (Fig. 1). The static parameters for complexes **1** and **2** are given in Table 2.



Scheme 1 Solution invertomers of the complexes $[ReX(CO)_3L^1]$ showing the hydrogen labelling

$[ReX(CO)_3L^2]$ (X = Cl, Br *or* I). The ambient-temperature solution NMR spectra of these complexes show the presence of two non-exchanging invertomer species. In these complexes, in contrast to the L^1 series, the species are present in similar abundance, presumably due to the reduced bulk of the thiomethyl as opposed to the *p*-tolyl group. The ^1H spectrum of $[ReCl(CO)_3L^2]$ at 20 °C in CD_2Cl_2 solution (Fig. 2) is typically

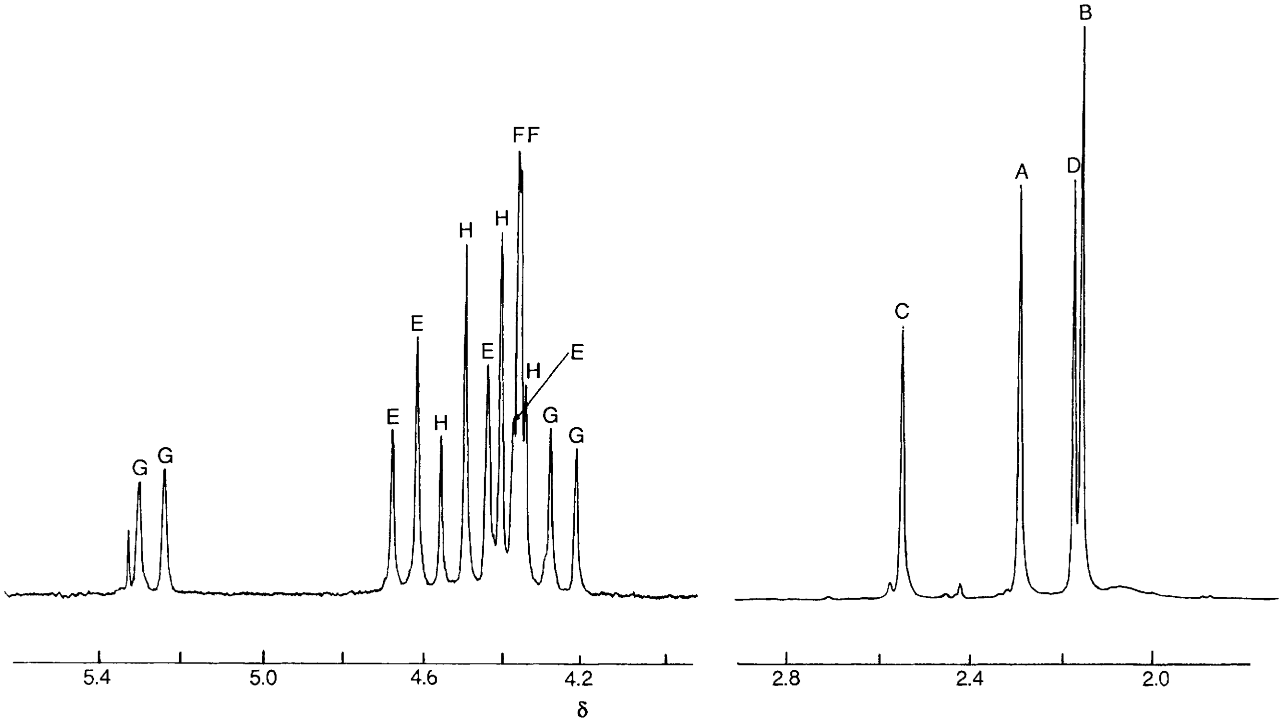


Fig. 2 The ^1H NMR spectrum of $[ReCl(CO)_3L^2]$ at 20 °C showing the ligand methyl and methylene regions. The labelling refers to Scheme 2

Table 2 Proton NMR parameters of complexes $[ReX(CO)_3L^1]$ at low temperature (−10 °C)

			Chemical shifts (δ)			
Complex	X	Invertomer population	Me	CH_2 [a]	Pyridine ring [b]	Phenyl [c]
1	Cl	0.81 (*trans*)	2.33, 2.31	5.49, 4.56 (15.0) 4.85, 4.63 (17.5)	7.76 (*m*), 7.54 (*m*), 7.43 (*p*) (7.65)	7.03–7.38
		0.19 (*cis*)	2.34, 2.30	5.29, 4.69 (15.0) 4.81, 4.75 (15.0)	*d*	
2	Br	>0.9 (*trans*)	2.36, 2.32	5.55, 4.62 (15.0) 4.83, 4.66 (17.5)	7.75 (*m*), 7.53 (*m*), 7.43 (*p*) (7.64)	6.97–7.37

[a] ^2J(HH)/Hz in parentheses. [b] ^3J(HH)/Hz in parentheses. [c] Aromatic region too complex for detailed analysis. [d] Precise shifts not clear due to overlap.

Table 3 Proton NMR parameters of complexes $[ReX(CO)_3L^2]$

				Chemical shifts (δ)		
Complex	X	T/°C	Invertomer population	SMe	CH_2[a]	Pyridine ring[b]
4	Cl	20	0.58 (*cis*)	2.27, 2.14	4.62, 4.39 (15.6), 4.43, 4.25 (16.0)	7.37–7.99
			0.42 (*trans*)	2.53, 2.15	5.25, 4.23 (15.8), 4.50, 4.36 (15.1)	
5	Br	30	0.51 (*cis*)	2.42, 2.15	4.65, 4.40 (15.4), 4.36, 4.31 (15.8)	7.34–7.97
			0.49 (*trans*)	2.56, 2.17	5.32, 4.31 (17.5), 4.51, 4.37 (15.1)	
6	I	30	0.26 (*cis*)	2.64, 2.15	4.67, 4.51 (15.2), 4.36, 4.26 (15.0)	7.27–7.88
			0.74 (*trans*)	2.60, 2.17	5.33, 4.45 (16.0), 4.44, 4.35 (16.0)	

[a] ^2J(HH)/Hz in parentheses. [b] Precise shifts not clear due to overlap.

Table 4 Best-fit rate constants used in the computer simulation of the NMR spectrum of $[ReBr(CO)_3L^2]$ **5**

T/°C	k_{inv}/s^{-1}	k_{exch}/s^{-1}	k'_{exch}/s^{-1}	k''_{exch}/s^{-1}
50	≈0	2.2	~0	2.2
60	4.4	4.4	4.4	4.4
80	18	23	17	23
85	26	30	28	
90		54	40	50
100	70	90	90	140
120	270		250	500

representative of the spectra for this series. Line assignments were based on similar arguments to those used for the L^1 series of complexes, and the spectral parameters for the methyl and methylene regions are given in Table 3. It will be seen here that the *trans* invertomer becomes more favoured as the mass/size of the halogen increases.

Above-ambient-Temperature NMR Studies.—$[ReCl(CO)_3L^1]$. Variable-temperature ^1H NMR experiments were carried out on this complex in CD_2Cl_2. As the solution was warmed from −10 °C changes occurred in all three regions of the spectra (Fig. 1). In the methyl region signals A and C coalesced as did B and D, leading to two sharp singlets at 40 °C. In the methylene region the AB quartets due to the non-equivalent methylenes of the chelate rings, CH_2^E and CH_2^G, coalesced to a single AB quartet and a similar coalescence occurred with the signals due to the pendant methylenes CH_2^F and CH_2^G (Scheme 1). These changes are clearly indicative of pyramidal inversion of the co-ordinated S atoms effecting an exchange between the *trans* and *cis* invertomers (Scheme 1). An NMR bandshape analysis was performed on the methyl and methylene signals and good agreement between experimental and computer-simulated bandshapes was obtained. For a given temperature both spectral regions were fitted with the same rate constant, confirming a single dynamic process. The Arrhenius and Eyring activation parameters for $[ReCl(CO)_3L^1]$ are $E_a = 91.8 \pm 5.5$ kJ mol^{-1}, $\log_{10}(A/s^{-1})$ 15.7 ± 0.9, $\Delta H^‡ = 89.2 \pm 5.5$ kJ mol^{-1}, $\Delta S^‡ = 46.3 \pm 17.4$ J K^{-1} mol^{-1} and $\Delta G^‡$ (298 K) = 75.4 ± 0.3 kJ mol^{-1}.

Similar studies on the complexes $[ReBr(CO)_3L^1]$ and $[ReI(CO)_3L^1]$ were not possible because the *cis* invertomer species were present in immeasurably low abundances.

The NMR solution spectra of $[ReCl(CO)_3L^1]$ were measured in $CDCl_2CDCl_2$ solvent when further changes were observed. In the methyl region the two averaged singlets first broadened then coalesced at *ca.* 75 °C and finally became a single sharp resonance. In the methylene region the two inversion-averaged AB quartets underwent mutual exchange to give a single averaged singlet. At 125 °C, the highest temperature studied, this band still exhibited some exchange broadening. In the aromatic region the signals due to the 2,6 and 3,5 protons of the *p*-tolyl ring simplified to two doublets, while for the pyridine ring the signal due to the 4-proton remained a sharp triplet but the 3- and 5-protons produced a broad featureless band. All these changes, which were reversible with temperature, are consistent with some intramolecular fluxional process which exchanges the co-ordinated and unco-ordinated *p*-tolylthiomethyl groups. When the process becomes fast on the NMR time-scale the fluxional species possesses effective C_s symmetry with the σ_h plane passing through the 4-hydrogen of the pyridine ring. This explains why the signal of this hydrogen is totally unaffected by the replacement process. Approximate activation energies, $\Delta G^‡(T_c)$/kJ mol^{-1}, for this fluxion were measured from the band coalescences in the methyl (76.2, 70 °C), methylene (75.7, lower-frequency portion, 90 °C; 81.4, higher-frequency portion, 120 °C) and pyridine regions (78.6, 105 °C) of the spectrum.

$[ReX(CO)_3L^2]$ (X = Cl *or* Br). On increasing the solution temperature the methylene and pyridine-ring regions of the NMR spectra exhibited dynamic exchange effects analogous to those of the L^1 complexes. At 130 °C, the highest temperature reached, a single averaged methylene AB quartet was observed, with the low-frequency arm quite well defined. The pyridine region at this temperature consisted of a sharp triplet due to the H^4 proton and a single broad band due to H^3 and H^5.

The MeS region was submitted to a full bandshape analysis. At ambient temperature the four signals are assigned unambiguously to the co-ordinated and unco-ordinated MeS of the *trans* and *cis* invertomers (Scheme 2). On raising the solution temperature of the complex $[ReCl(CO)_3L^2]$ the four MeS signals exhibited exchange broadening and coalesced to a single band at *ca.* 110 °C. The bandshape changes suggest concurrent pyramidal sulfur inversion and intramolecular exchange of the MeS groups (Fig. 3).

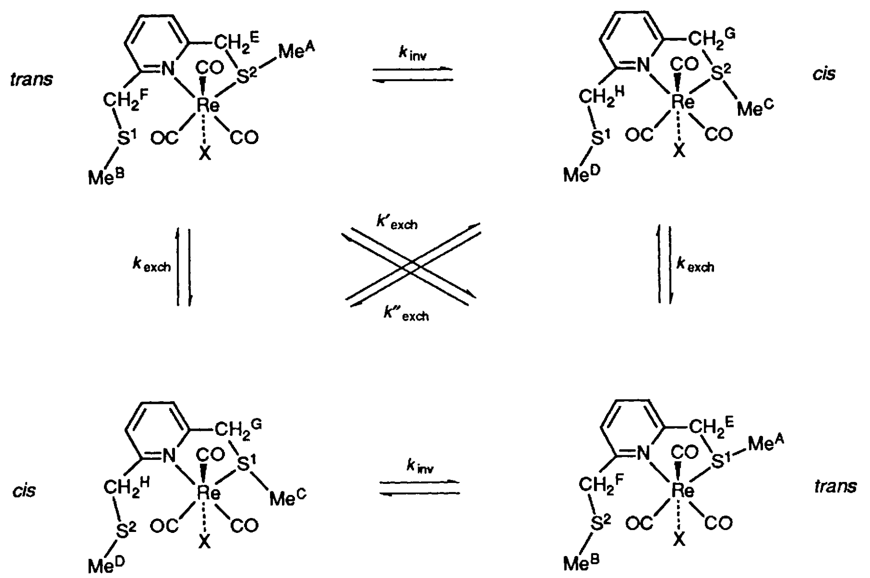
The dynamics of such a combination of processes are represented by four types of rate constant. The sulfur-inversion rate constants k_{inv} define *cis–trans* exchange without MeS exchange, whereas co-ordinated–unco-ordinated MeS exchange is represented by three rate constants, namely k_{exch} when the exchange involves *cis–trans* interconversion, k'_{exch} for *trans–trans* exchange and k''_{exch} for *cis–cis* exchange (Scheme 2).

For complex **4** (X = Cl) the dynamic NMR spectra could be fitted satisfactorily using a single magnitude of rate constant for each temperature. That implies that the sulfur inversion rate cannot be separated from the MeS exchange process and only the composite dynamics can be measured. For complex **5** (X = Br) good fittings of experimental and computer-simulated spectra could be achieved only when the four types of rate constants were treated as independent variables, even though for a given temperature their magnitudes do not differ greatly (Table 4). Arrhenius and Eyring activation parameters for both complexes **4** and **5** are given in Table 5.

Discussion

There are two interesting discussion points arising from the findings of these dynamic NMR studies, namely the magnitudes of the energy barriers for these internal molecular motions and the mechanism of the thioalkyl or thioaryl replacement process.

The energy data in the text and Table 5 indicate a striking



Scheme 2 Solution invertomers of the complexes $[ReX(CO)_3L^2]$ showing the interconversion pathways resulting from sulfur inversion and MeS exchange processes

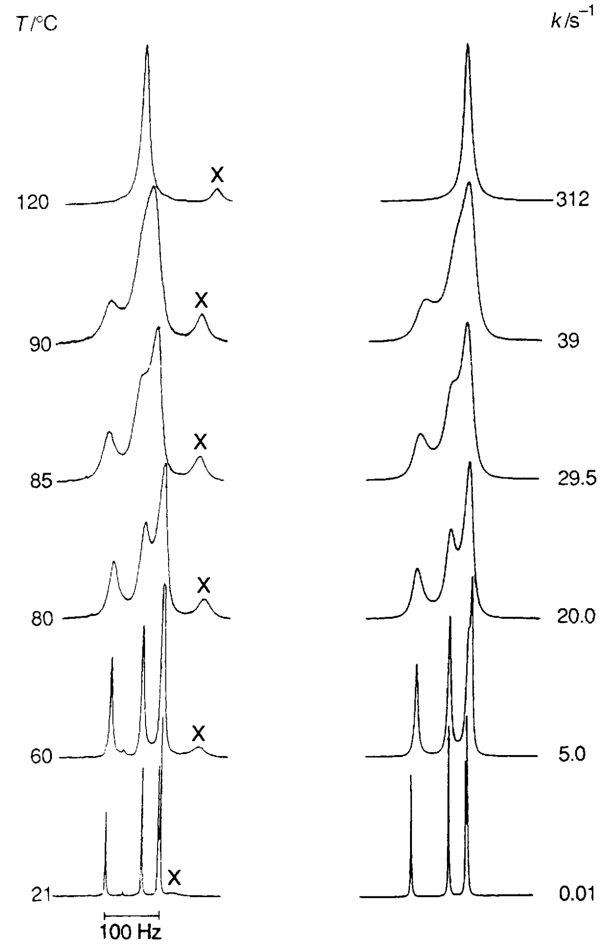


Fig. 3 Experimental and computer-synthesised ^1H NMR spectra of $[ReCl(CO)_3L^2]$ (SMe region only) showing the 'best fit' average rate constant for each temperature. Band marked X is an impurity

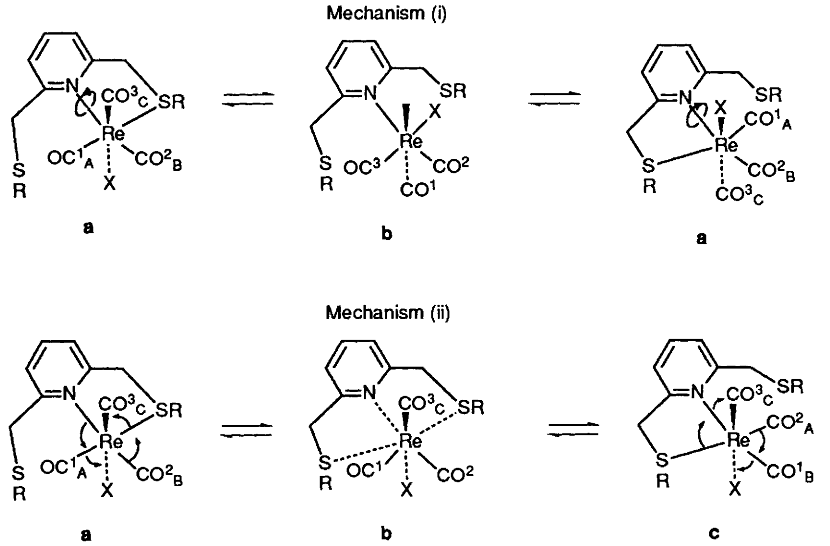
similarity between the pyramidal sulfur inversion and replacement process. Indeed, for complexes **4** and **5** the energy values are the same within experimental uncertainty. This suggests that the Re–S bond weakening arising from pyramidal sulfur inversion is sufficient to initiate the sulfur exchange process. The $\Delta G^‡$ values for either process (75–81 kJ mol^{-1}) are exceptionally large, particularly for the inversion process. For related $[ReX(CO)_3L]$ complexes involving five-membered chelate rings, sulfur inversion energies while being fairly independent of halide X vary with L as follows [$\Delta G^‡$ (298 K) values in parentheses]: L = $MeSCH_2CH_2SMe$ (63.9–66.7 kJ mol^{-1}),[10] MeSCH=CHSMe (51.8–58.1 kJ mol^{-1}),[10] *o*-$MeSC_6H_4SMe$ (53.5–56.4 kJ mol^{-1})[11] and *o*-$MeSC_6H_4PPh_2$ (51.7–53.6 kJ mol^{-1}).[2] Clearly, these values are substantially lower than the new values, particularly when the inverting sulfur is attached to an olefinic or aromatic centre. When bonded to an aliphatic CH_2 group as in $MeSCH_2CH_2SMe$ and the present complexes the inversion energy is significantly greater. Indeed, the latest values would appear to be the highest reported for pyramidal inversion of metal-co-ordinated S atoms. These values imply greater strain in these unsymmetrical S/N heterocyclic rings compared to the more symmetrical S/S rings. The energies for the thioalkyl or thioaryl replacement process appear to be essentially independent of the group attached to sulfur, and are appreciably higher than the MeS replacement process observed in the complexes $[M\{PPh(C_6H_4SMe\text{-}o)_2\}X_2]$ (M = Pd or Pt).[3] The difference here, however, probably reflects the different electronic influences of the $Pd^{II}X_2$ or $Pt^{II}X_2$ moieties compared to $ReX(CO)_3$ on the inverting sulfur centre.

Two possible mechanisms for the thioalkyl or thioaryl replacement process can be envisaged. These are depicted in Scheme 3. Mechanism (*i*) involves a loosening of the Re–S bond as a result of pyramidal sulfur inversion followed by rotation about the Re–N bond through an angle of 180° to produce the original structure **a**. An analogous rotation mechanism was assumed to occur in the complexes $[M\{PPh(C_6H_4SMe\text{-}o)_2\}X_2]$ (M = Pd or Pt; X = Cl, Br or I).[3] Here, however, the process involved rotation about the M–P bond through the tetrahedral angle (109° 58′) in order to bring the pendant MeS close enough for participation in a five-co-ordinate metal transition state, and thence to displace the bound MeS. Whilst such a rotation mechanism is the most plausible explanation of the fluxion in those mixed-phosphine metal complexes, the operation of an analogous mechanism in the present N/S complex is far less certain. This is mainly due to the much larger angle of rotation involved and the steric congestion of the halide with one of the thio-alkyl or -aryl groups in the 90° transition state structure **b** in mechanism (*i*). [This congestion, however, could be relieved somewhat by a concerted rotation about the S(R)–CH_2 bond.] The alternative mechanism, (*ii*), involves a twist of the whole $ReX(CO)_3$ moiety about its X–Re–CO axis through an angle

Table 5 Activation parameters for the dynamic processes in the complexes [ReX(CO)$_3$L^2] (X = Cl or Br)

Complex	X	Process	E_a/ kJ mol^{-1}	$\log_{10}(A/s^{-1})$	$\Delta H^‡$/ kJ mol^{-1}	$\Delta S^‡$/ J K^{-1} mol^{-1}	$\Delta G^{‡a}$/ kJ mol^{-1}
4	Cl	k_{av}[b]	74.6 ± 1.31	12.4 ± 0.2	71.7 ± 1.3	−18.0 ± 3.6	77.1 ± 0.2
5	Br	k_{inv}	74.6 ± 1.8	12.3 ± 0.3	71.6 ± 1.8	−19.1 ± 4.9	77.3 ± 0.3
		k_{exch}	76.4 ± 2.4	12.7 ± 0.4	73.5 ± 2.4	−12.2 ± 6.9	77.1 ± 0.4
		k'_{exch}	75.1 ± 2.7	12.4 ± 0.4	72.1 ± 2.7	−17.4 ± 7.4	77.3 ± 0.5
		k''_{exch}	83.4 ± 2.8	13.8 ± 0.4	80.5 ± 2.8	8.7 ± 7.8	77.9 ± 0.4

[a] At 298.15 K. [b] Each temperature fitted to one rate constant (see text).



Scheme 3 The two possible mechanisms for the S-alkyl or S-aryl exchange fluxion. The rotation mechanism (*i*) is depicted as the ReX(CO)$_3$ moiety rotating whereas in Scheme 2 the ligand rotates relative to ReX(CO)$_3$. Both descriptions are equivalent. The 'tick-tock' twist mechanism (*ii*) is shown to exchange the equatorial rhenium carbonyl environments A and B, unlike mechanism (*i*)

equal to the N–Re–S angle. It requires simultaneous loosening of both the Re–N and Re–S bonds and involves a seven-co-ordinate rhenium intermediate or transition-state structure in which both S and the N atom contribute to the bonding, structure **b**. This mechanism involves far less relative movement of the ligand and metal moieties and the intermediate structure is not sterically hindered. A very analogous fluxion was shown recently[12,13] to occur in the complexes [PtXMe$_3$(terpy)] (X = Cl, Br or I; terpy = 2,2′:6′,2″-terpyridine). A similar fluxion was detected for [ReX(CO)$_3$(terpy)] (X = Cl, Br or I)[12,13] and an analogous mechanism proposed. The main difference between this 'tick-tock' twist mechanism[12] in these terpyridine complexes and in the present complexes is that in the former only one type of bond (M–N) is involved in the breaking/remaking process in contrast to the two (M–N and M–S) in the present complexes. Substantially stronger Re–N compared to Re–S bonding would obviously favour the rotation mechanism which does not involve any Re–N bond scission. If the Re–N and Re–S bond strengths are of comparable magnitude, then the 'tick-tock' twist mechanism would be clearly favoured. It is pertinent to note at this point that the energy barriers [$\Delta G^‡$ (298 K)] for this fluxion in the present complexes (75–81 kJ mol^{-1}), are of comparable magnitude to that found for the metal moiety twist fluxion in the complex [ReBr(CO)$_3$(terpy)] [$\Delta G^‡$ (298 K) = 71.6 kJ mol^{-1}][12] which is clearly suggestive of a similar mechanism.

Distinction between these two mechanisms is theoretically possible as has been demonstrated in the case of the complexes [PtXMe$_3$(terpy)].[12,13] The rotation mechanism (*i*) produces no exchange of the two groups attached to the metal in the equatorial positions, namely carbonyls CO^1 and CO^2 in the present complexes. In contrast, the twist mechanism will produce such an exchange as indicated in Scheme 3 by the interchange of their chemical environments A and B. The different effects of the two mechanisms on the equatorial positions are reflected in the fact that the resulting structures for each process, **a** in (*i*) and **c** in (*ii*), are not identical but constitute a DL pair. Clearly, variable-temperature ^{13}C NMR spectra of the carbonyl signals of these complexes should provide the necessary verifying information. Unfortunately, to date the limited quantities and solubilities of these complexes have precluded such measurements.

Further insight into this problem should be possible by synthesising the trimethylplatinum(IV) halide complexes of the present ligands, namely [PtXMe$_3$L^1] and [PtXMe$_3$L^2], and deducing the mechanism for the likely thioalkyl or thioaryl replacement fluxion by the presence or absence of equatorial PtMe exchange. This would establish the definitive mechanism for the process in the same way as was achieved for the [PtXMe$_3$(terpy)] complexes.[12,13] We are currently engaged on such work.

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