NMR Investigations of Restricted Rotations and Metallotropic Shifts in Rhenium(I) Tricarbonyl Halide Complexes of Pyridyl Carboxamide and Thioamide Ligands

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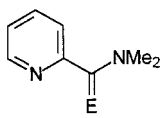
A series of rhenium(I) tricarbonyl halide complexes of pyridyl mono- and di-carboxamides and -thioamides has been studied by dynamic NMR techniques. Oxygen coordination to Re^{I} of the carboxamide ligand reduced the energy barrier to C−N rotation by 2−13 kJ mol^{-1} whereas sulfur−Re^{I} coordination of the thioamide ligands led to a reduction of 28−33 kJ mol^{-1}. In the pyridyl dicarboxamide and -dithioamide metal chelate complexes metallotropic shifts occur between the three donor atoms, O, N, O or S, N, S, energies [$\Delta G^{\ddagger}$ (298.15 K)] being in the range 78−89 kJ mol^{-1}; these high values arise from the strong electron donating properties of the -NR2 (R = Me, Et) groups.

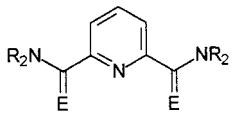
Introduction

As part of a research programme into the coordination properties of terdentate ligands and the molecular dynamics in solution of the metal complexes that are formed when the ligand is acting as a bidentate chelate ligand to a metal, we have previously investigated some metal complexes formed by ligands such as 2,2′:6′,2′′-terpyridine(terpy)[1] and 2,6-bis(pyrazol-1-yl)pyridine (bppy)[2] that present a N_3 donor set to the metal moieties. From these studies we have obtained quantitative information on the mechanisms and energetics of molecular motions such as 1,4-metallotropic shifts,[3] and metal-hurdling[4] fluxions. In order to investigate potential electronic and steric effects on the structures and dynamic behaviour in solution of related ligands and the corresponding metal complexes we have initiated an investigation into some complexes formed by pyridine-based terdentate ligands that present an ONO or a SNS donor set to a metal. In this paper we report our findings for the synthesis and studies by the methods of dynamic NMR spectroscopy on the carboxamide and thioamide ligands, *N*,*N*-dimethyl-2-pyridinecarboxamide (dmpc), *N*,*N*-dimethyl-2-pyridinethioamide (dmpt), *N*,*N*,*N*′,*N*′-tetramethyl-2,6-pyridinedicarboxamide (tmpdc), *N*,*N*,*N*′,*N*′-tetramethyl-2,6-pyridinedithioamide (tmpdt), *N*,*N*,*N*′,*N*′-tetraethyl-2,6-pyridinedicarboxamide (tepdc), *N*,*N*,*N*′,*N*′-tetraethyl-2,6-pyridinedithioamide (tepdt) and the metal complexes [$ReX(CO)_3L$] (X = Cl or Br; L = dmpc, dmpt, tmpdc, tmpdt or tepdc).

The dicarboxamide compounds have previously been used as ligands for complex formation with the lanthanide elements[5][6] and with cobalt(II), copper(II) and nickel(II) of the d-block metals.[7,8,9] In all the metal complexes studied previously the ligands are acting in a terdentate chelate mode that uses the pyridyl nitrogen and the two oxygen atoms as the donor set. To the best of our knowledge the thioamides have not been employed as ligands.



E = O dmpc
E = S dmpt



E = O, R = Me tmpdc
E = O, R = Et tepdc
E = S, R = Me tmpdt
E = S, R = Et tepdt

When the pyridyl dicarboxamide and dithioamide ligands act as bidentate chelates they may be described as hemilabile ligands.[10] Such ligands contain at least two different types of bonding group with different bonding strengths and these can lead to intramolecular ligand exchange processes ("fluxional shifts") and ligand displacement reactions. The coordination chemistry of such ligands has recently been reviewed.[11] This present work is a further contribution to this active area of chemistry.

Results

The carboxamide and thioamide ligands were prepared as described in the experimental section. The monofunctional ligands were air-stable oils and the difunctional ligands air-stable, crystalline solids. The rhenium(I) complexes of the ligands, namely *fac*-[$ReX(CO)_3L$] (X = Cl, L = tmpdc, tepdc, or tmpdt; X = Br, L = dmpc, tmpdc, tepdc, dmpt or tmpdt) were isolated in good yields as yellow or orange/red air-stable solids. The ligands and their Re^{I} complexes were characterised by melting point, IR and ^1H NMR spectroscopy, EI mass spectrometry, and, in the case of the metal complexes, by elemental analysis (Table 1).

In the metal carbonyl stretching region of the infrared spectra the complexes show three strong peaks (Table 1) consistent with a facial arrangement of the carbonyl groups.[1]

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Table 1. Synthetic and analytical data for the Re^{I} complexes of pyridyl mono- and di-carboxamides and -thioamides

Complex	M.p./°C	% Yield[a]	$\tilde{\nu}$(CO)[b]/cm^{-1}	Analysis[c] (%)		
				C	H	N
[ReBr(CO)$_3$dmpc]	172 dec.	93	2026, 1917, 1895	26.6(26.4)	2.0(2.0)	5.6(5.6)
[[ReBr(CO)$_3$dmpt]	215 dec.	94	2027, 1933, 1900	25.8(25.6)	1.9(2.0)	5.4(5.4)
[ReCl(CO)$_3$tmpdc]	256 dec.	96	2027, 1920, 1901	32.2(31.9)	2.7(2.9)	7.9(8.0)
[ReBr(CO)$_3$tmpdc]	259 dec.	79	2028, 1921, 1901	29.4(29.4)	2.5(2.7)	7.1(7.4)
[ReCl(CO)$_3$tmpdt]	220 dec.	96	2028, 1930, 1908	30.9(30.1)	2.5(2.7)	7.4(7.5)
[ReBr(CO)$_3$tmpdt]	250 dec.	95	2028, 1931, 1906	28.4(27.9)	2.3(2.5)	6.9(7.0)
[ReCl(CO)$_3$tepdc]	218 dec.	67	2022, 1902, 1890	37.0(37.1)	3.8(3.9)	7.1(7.2)
[ReBr(CO)$_3$tepdc]	221 dec.	47	2010, 1905, 1880	34.4(34.5)	3.5(3.7)	6.4(6.7)

[a] Yield quoted relative to metal-containing reactant. – [b] Recorded as chloroform solution. – [c] Calculated values in parentheses.

This indicates that the pyridine-based ligands are acting as bidentate chelate ligands by substituting two equatorial carbonyl groups of the [ReX(CO)$_5$] compound. For the complexes derived from the dicarboxamide ligands two amide carbonyl stretching vibrations are observed in the infrared spectrum, one approximating to the free ligand value and the other 25–30 cm^{-1} lower. This observation indicates that the dicarboxamide ligands are bound to the metal in a bidentate chelate fashion via an ON donor set. This finding was confirmed by the ^{1}H NMR spectroscopic studies (see later).

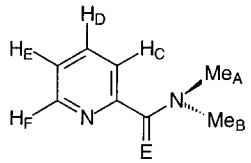
(i) Monoamide ligands, (L), dmpc, dmpt and Complexes [ReBr(CO)$_3$L]

The ^{1}H NMR spectra of dmpc and dmpt consisted of six signals (Table 2), the pairs of *N*-methyl shifts indicating severe restriction to rotation about the C–N bond of the carboxamide and thioamide functions. This is fully in accordance with previous studies of such systems and, in particular, on dmpc.[12] Distinction between the *N*-methyl signals was based on the results of the NOE difference experiments (carried out on the corresponding dicarboxamides tmpdc and tepdc, see later).

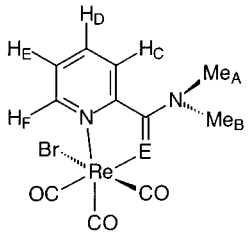
The energy barrier to rotation in dmpc was measured by obtaining ^{1}H NMR spectra in the temperature range 303–373 K. On increasing the temperature the two *N*-methyl signals broadened, coalesced (at 363 K) and then changed to a single, sharp signal. A bandshape analysis of signals in the range 323–373 K yielded an activation energy (see later) in good agreement with a previous study.[12] In contrast, variable temperature ^{1}H NMR spectra of the thioamide dmpt showed no signal broadening up to ca. 393 K, indicating that the rate of C(S)–N bond rotation was slow on the NMR timescale even at 393 K. The 2D-EXSY NMR method,[13–15] which is sensitive to slower exchange rates that are not accompanied by any line broadening, was therefore applied in the temperature range 353–393 K with mixing times 0.8 s (353 K), 0.1 s (373 K) and 0.02 s (393 K). Clear cross-peaks between the *N*-methyl signals were observed at these temperatures, from which first-order rate constants for the bond rotation process were computed with the authors' D2DNMR program.[27]

Coordination of dmpc and dmpt to form ReBr(CO)$_3$ complexes led to strikingly different room temperature ^{1}H NMR spectra. These are shown in Figure 1, where it will be noted that [ReBr(CO)$_3$dmpc] shows a clear chemical shift

Table 2. ^{1}H NMR spectroscopic data for the ligands dmpc, dmpt and the complexes [ReBr(CO)$_3$L] (L = dmpc, dmpt)



E = O, S



E = O, S

Compound	δ_A	δ_B	δ_C (J_{CD}/Hz)	δ_D (J_{CD}, J_{DE}/Hz)	δ_E (J_{DE}, J_{EF}/Hz)	δ_F (J_{EF}/Hz)
dmpc[a]	3.03 s	3.11 s	7.57 d (7.6)	7.35 t (7.6, 7.6)	7.80 dd (7.6, 5.0)	8.65 (broad)[c]
dmpt[b]	3.16 s	3.58 s	7.56 d (8.0)	7.22 t (8.0, 8.0)	7.70 dd (7.0, 4.0)	8.48 s (broad)[c]
[ReBr(CO)$_3$dmpc][a]	3.36 s	3.56 s	8.04 d (8.0)	7.70 t (8.0, 8.0)	8.14 dd (8.0, 6.6)	9.10 d (6.7)
[ReBr(CO)$_3$dmpt][b]	3.67 s	3.67 s	7.55 d (8.0)	7.47 t (8.0, 8.0)	7.98 dd (8.0, 6.2)	9.10 d (6.2)

[a] Measured in $(CDCl_2)_2$ at 303 K relative to Me_4Si (δ = 0). – [b] Measured in $CDCl_3$ at 303 K relative to Me_4Si (δ = 0). – [c] Due to ^{14}N quadrupole broadening. s = singlet, d = doublet, dd = doublet of doublets, t = 1:2:1 triplet.

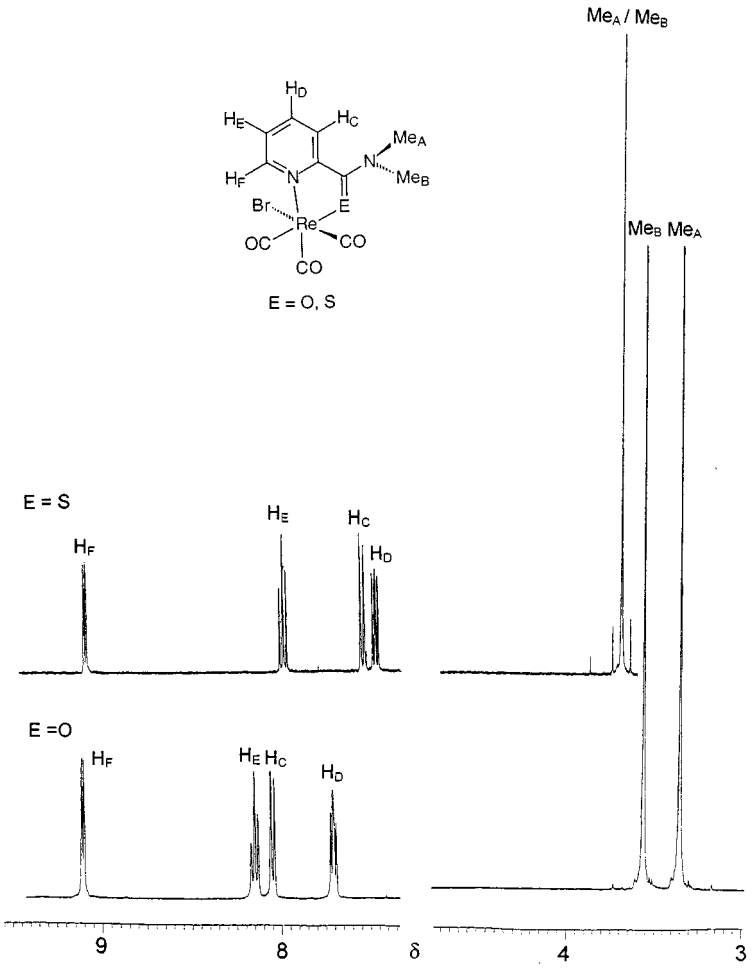
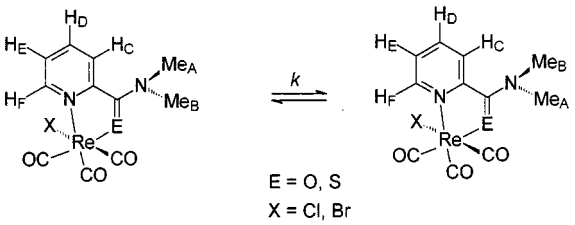


Figure 1. 400 MHz ^{1}H NMR spectra of [ReBr(CO)$_3$dmpc] and [ReBr(CO)$_3$dmpt] at 303 K in $(CDCl_2)_2$ and $CDCl_3$ respectively

distinction between the *N*-methyl signals, whereas [ReBr(CO)$_3$dmpt] does not, implying that C−N rotation in the carboxamide complex is slow on the NMR timescale at ambient temperatures whereas in the thioamide it is fast.

The temperature dependencies of these exchange rates, *k*, described according to Scheme 1, were measured by recording the ^{1}H NMR spectra of [ReBr(CO)$_3$dmpc] in the range 303−413 K and of [ReBr(CO)$_3$dmpt] in the range 223−303 K. Coalescences of the pairs of *N*-methyl signals in these two complexes occurred at ca. 363 K and ca. 268 K, respectively. Bandshape analyses in these temperature ranges enabled energy barriers for the C−N rotations to be evaluated (see later).



Scheme 1. Restricted rotation of the NMe_2 group in the monoamide ligand complexes

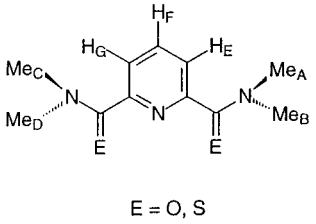
(ii) Diamide ligands (L) tmpdc, tmpdt, and Complexes [ReX(CO)$_3$L] (X = Cl, Br)

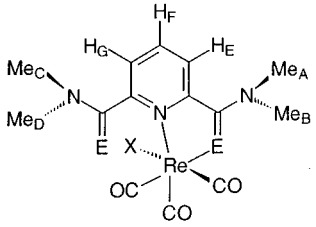
The ligands tmpdc and tmpdt exhibited ^{1}H NMR spectral features (Table 3) very similar to their monofunctional counterparts dmpc and dmpt. Thus, at ambient temperatures both ligands displayed chemical shift distinction within each of the *N*/*N*′-dimethyl pairs. Unambiguous assignments were made with the aid of Nuclear Overhauser Enhancement (NOE) difference experiments on tmpdc.

Irradiation of the lower frequency methyl signal at δ = 3.07 caused a positive NOE of the pyridyl $H_{E/G}$ signal whereas no such effect was observed on irradiating the signal at δ = 3.15. The NOE was small indicating that the NMe_2 groups are not coplanar with the ring but rotated such that the methyls Me_A/Me_C are in shielding zones associated with the aromatic ring current.

On warming, exchange broadening of the *N*-methyl signals occurred in the case of tmpdc, with coalescence being achieved at ca. 353 K, whereas no significant broadening occurred for tmpdt until ca. 393 K, which was near the high-temperature limit of the solvent $(CDCl_2)_2$. The 2D-EXSY method was therefore used for tmpdt, and good quality, rate-sensitive spectra achieved at temperatures 353,

Table 3. ^{1}H NMR spectroscopic data for the ligands tmpdc, tmpdt and the complexes [ReX(CO)$_3$L] (L = tmpdc, tmpdt; X = Cl, Br)





Compound	δ_A	δ_B	δ_C	δ_D	δ_E (J_{EF}/Hz)	δ_F (J_{EF}, J_{FG}/Hz)	δ_G (J_{FG}/Hz)
tmpdc[a]	3.07 s	3.15 s	3.07 s	3.15 s	7.65 d (7.7)	7.92 t (7.7, 7.7)	7.65 t (7.7)
tmpdt[b]	3.19 s	3.58 s	3.19 s	3.58 s	7.51 d (7.8)	7.77 t (7.8, 7.8)	7.51 d (7.8)
[ReCl(CO)$_3$tmpdc][a]	3.35 s	3.55 s	2.98 s	3.23 s	7.96 d (7.5)	8.18 t (7.9, 7.9)	7.65 d (7.5)
[ReBr(CO)$_3$tmpdc][a]	3.32 s	3.53 s	2.99 s	3.22 s	7.94 d (8.1)	8.19 t (7.9, 7.9)	7.65 d (8.0)
[ReCl(CO)$_3$tmpdt][b]	3.65 s	3.65 s	3.18 s	3.64 s	7.50 d (10.5)	8.02 t (10.5, 10.5)	7.38 d (10.5)
[ReBr(CO)$_3$tmpdt][b]	3.63 s	3.63 s	3.20 s	3.64 s	7.44 d (10.6)	7.95 t (10.6, 10.6)	7.31 d (10.5)

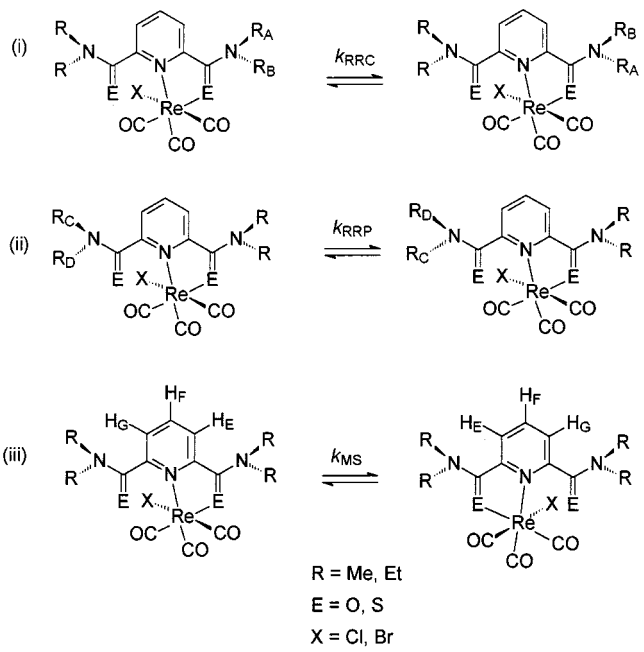
[a] Measured in $(CDCl_2)_2$ at 303 K. – [b] Measured in $CDCl_3$ at 303 K. s = singlet, d = doublet, t = triplet.

373 and 393 K, using mixing times of 0.5 s, 0.1 s and 0.01 s, respectively. The spectral characteristics of both these ligands indicate the very different degrees of restriction to C–N rotation in these species.

The ^{1}H NMR spectra of [ReX(CO)$_3$tmpdc] (X = Cl, Br) consisted of four separate *N*-methyl signals, the pair Me_A/Me_B associated with the coordinated carboxamide group being to high frequency of the other pair, Me_C/Me_D. On warming the $(CDCl_2)_2$ solution of the complex the signals of Me_A and Me_B began to broaden, coalescing at ca. 343 K and then sharpening to an averaged signal. The signals of Me_C and Me_D showed slight increases in bandwidth above ca. 323 K, indicating the onset of slow C–N rotation in the pendant – $C(O)NMe_2$ group as well as in the coordinated group. This broadening increased with increasing temperature until at ca. 403 K the Me_C/Me_D signals started to merge with the broad average Me_A/Me_B signal. By 413 K all signals had coalesced into a single broad signal. These changes are clearly indicative of the consecutive onset of (i) C–N rotation of the coordinated -$C(O)NMe_2$ group, (ii) C–N rotation of the pendant -$C(O)NMe_2$ group, and (iii) 1,4-metallotropic shifts which cause a loss of distinction between the coordinated and uncoordinated carboxamide functions. Further evidence for the 1,4-metallotropic shift was obtained from the signals of the pyridyl hydrogens at the 3- and 5-position (labelled H_E and H_G). These commenced broadening at 343 K and by 413 K had almost coalesced to a very broad band envelope with half-height width of ca. 100 Hz.

These spectral changes can be interpreted in terms of the exchanges depicted in Schemes 2 (i) – (iii) (E = O; R = Me).

Rate data for these schemes were obtained by bandshape analysis of the *N*-methyl region spectra in the temperature range 303–353 K for the C–N rotation rates (for coordinated and pendant groups) and the pyridyl hydrogen region spectra in the range 343–413 K for the 1,4-metallotropic shifts.



Scheme 2. Three types of internal dynamic process in the diamide ligand complexes

The room temperature ^{1}H NMR spectra of the complexes [ReX(CO)$_3$tmpdt] (X = Cl, Br) exhibited three *N*-methyl signals in the intensity ratio 6:3:3. The signal of intensity 6 was due to the *N*-methyl groups of the coordi-

nated thioamide group which rotates rapidly on the NMR timescale, while the signals of intensity 3 were due to the chemically distinct *N*-methyls of the uncoordinated -C(S)NMe_2 group where C−N rotation was slow on the NMR timescale, as was observed in the free ligand tmpdt. The rates of C−N rotation in the coordinated thioamide group were measured from spectra taken in the temperature range 263−313 K, with band coalescence occurring at ca. 288 K. Measurement of C−N rotation rates in the pendant -C(S)NMe_2 group required above-ambient temperature studies. Spectra measured in the range 383−413 K showed line broadenings but band coalescence was clearly above 413 K, the upper temperature limit of the solvent $(CDCl_2)_2$. Bandshape analysis of these line broadenings was dependent on the two rate constants k_{RRP} and k_{MS} (Scheme 2, E = S; R = Me); the latter, however, were most accurately measured from the effect of the metallotropic shifts on the H_E and H_G pyridyl hydrogens.

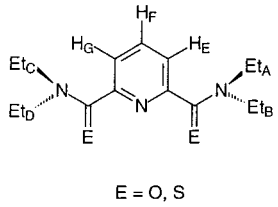
(iii) Ligands tepdc, tepdt and Complexes [ReX(CO)$_3$tepdc] (X = Cl, Br)

These ligands are the *N*,*N*,*N*′,*N*′-tetraethyl analogues of tmpdc and tmpdt and they behave in a very similar fashion. Their ^{1}H NMR characteristics are given in Table 4 where it will be observed that distinction within each of the pairs of *N*,*N*′-diethyl groups is seen in both the CH_2 and CH_3 signals.

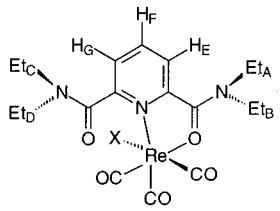
For tepdc unambiguous assignments of the CH_2 and CH_3 signals were made by NOE difference experiments. Irradiation of the CH_2 signal at δ = 3.35 caused a weak enhancement of the pyridyl hydrogens at the 3- and 5-positions whereas irradiation at the other CH_2 signal (δ = 3.55) caused no enhancement. The weakness of the enhancement indicated that the NEt_2 groups were considerably out of the pyridyl ring plane with the Et_A and Et_C groups shielded (relative to Et_B/Et_D) by the aromatic ring current. The NOEs of the methyl signals provided firm assignments of these signals also. It should be noted that all these assignments are rather at variance with those previously reported for tepdc[5] but in that study only a planar structure for this ligand was considered. However, molecular mechanics calculations on tepdc[8] have shown that the carbonyl groups of the carboxamide functions are twisted relative to the pyridine ring by ca. 64°. Such a twist accounts for the NOE effects between the methyl groups of Et_A and Et_C and the pyridyl hydrogens H_E and H_G being small, with these ethyl groups being shielded relative to Et_B and Et_D, since the latter are more remote from the effects of the pyridyl ring current. On raising the solution temperature of tepdc from 303 to 413 K, dynamic broadening occurs with coalescences at ca. 353 K (CH_3 signals) and ca. 360 K (CH_2 signals). Bandshape fittings of both sets of signals were made for six spectra in the temperature range 333−383 K, and provided reliable rate data.

The 2D-EXSY method had to be applied to the thioamide analogue tepdt to obtain rate data. Accordingly, 2D-EXSY spectra of tepdt were measured at 353, 373 and 393 K with mixing times of 0.8 s, 0.1 s and 0.01 s, respectively, and rate data obtained with the D2DNMR program.[27]

Table 4. ^{1}H NMR spectroscopic data for the ligands tepdc, tepdt and the complexes [ReX(CO)$_3$tepdc] (X = Cl, Br)



E = O, S



X = Cl, Br

Compound	δ(Et_A)		δ(Et_B)		δ(Et_C)		δ(Et_D)		δ_E	δ_F	δ_G
	CH_2	CH_3	CH_2	CH_3	CH_2	CH_3	CH_2	CH_3	(J_{EF}/Hz)	(J_{EF}, J_{FG}/Hz)	(J_{FG}/Hz)
tepdc[a]	3.35	1.16	3.55	1.27	3.35	1.16	3.55	1.27	7.62 (7.8)	7.91 (7.8, 7.8)	7.62 (7.8)
tepdt[a]	3.44	1.22	4.10	1.41	3.44	1.22	4.10	1.41	7.44 (7.8)	7.79 (7.8, 7.8)	7.44 (7.8)
[ReCl(CO)$_3$tepdc][b]	c	1.38	c	1.54	c	1.18	c	1.33	7.87 (7.8)	8.19 (7.9, 7.9)	7.62 (7.8)
[ReBr(CO)$_3$tepdc][b]	d	1.40	d	1.54	d	1.17	d	1.35	7.86 (7.9)	8.18 (8.0, 7.9	7.62 (7.8)

[a] Measured in $(CDCl_2)_2$ at 303 K. − [b] Measured in $(CDCl_2)_2$ at 273 K. − [c] Signals at δ = 4.25, 3.95*, 3.73*, 3.64*, 3.62*, 3.30, 3.27 and 3.08 (* coordinated side). − [d] Signals at δ = 4.24, 3.96*, 3.69*, 3.61*, 3.61*, 3.32, 3.29 and 3.08 (* coordinated side).

The ambient temperature ^{1}H NMR spectra of the complexes [ReX(CO)$_3$ tepdc] (X = Cl, Br) revealed some interesting features. Four distinct ethyl environments were identified as expected for a static bidentate chelate complex. These were represented by four methyl signals, two of which were sharp 1:2:1 triplets and two were broad, unsplit signals. On cooling to 273 K all four signals became sharp triplets (Figure 2).

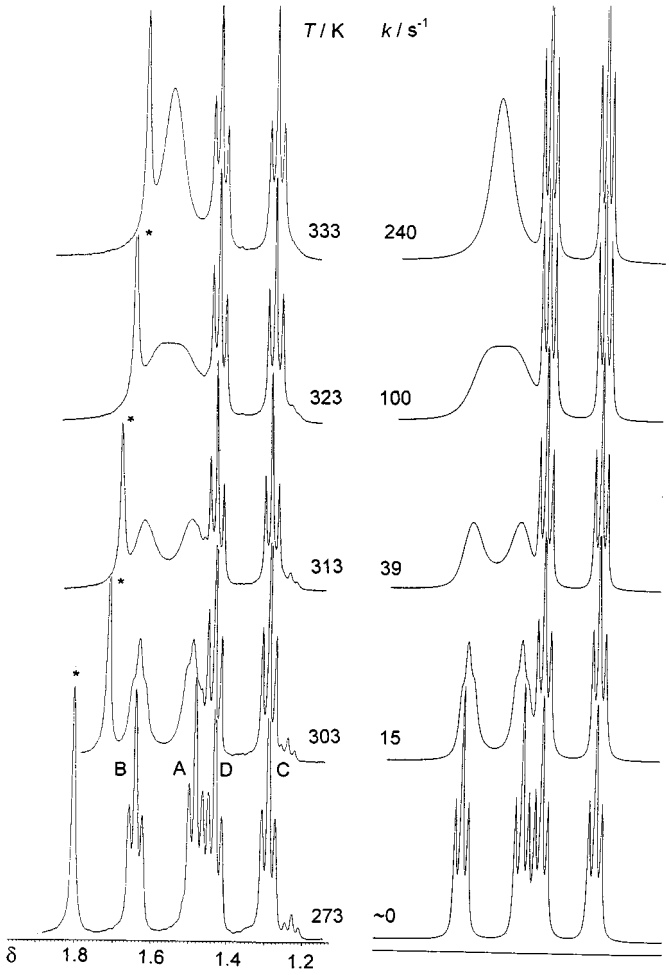


Figure 2. Variable temperature 400 MHz ^{1}H NMR spectra of [ReBr(CO)$_3$tepdc] in $(CDCl_2)_2$ showing the effects of restricted C−N rotation in the coordinated C(O)NEt$_2$ on the methyl signals; computer simulated spectra with "best-fit" rate constants are shown alongside. * solvent band

At 303 K the methylene hydrogens were represented by eight signals, four of which showed dynamic broadening and four which were sharp sextuplets. On cooling to 273 K all eight signals showed this same multiplet splitting which was interpreted as a combination of two-bond geminal methylene couplings and weaker three-bond couplings to the adjacent methyl hydrogens. The sextuplets resulting from partial overlap of the expected doublet of quadruplets had lines in the intensity ratio 1:3:4:4:3:1 and were the result of the $^2J_{HH}$ values being approximately twice the magnitude of the $^3J_{HH}$ values, (*viz*. $|^2J_{HH}| \approx 14$ Hz, $|^3J_{HH}| \approx 7$ Hz). The observation of spin-spin coupling between the geminal methylene hydrogens arises from the diastereotopic nature of these groups, which is not apparent in the free ligand.

The broadened signals in both the methyl and methylene regions of the spectra at room temperature are due to the ethyl environments A and B associated with the Re-coordinated -C(O)NEt$_2$ group. On warming, the broad methyl signals coalesced (at ca. 323 K for X = Br) and then the averaged signal sharpened. The four broadened methylene signals exhibited coalescences at ca. 313 K and 333 K, (X = Br). Bandshape analysis was performed on the methyl signals in the temperature range 273−373 K and excellent fits of experimental and theoretical spectra obtained (Figure 2), which led to activation energies for the restricted C−NEt$_2$ rotation on the metal-coordinated side.

On raising the temperature beyond 333 K additional dynamic broadenings involving all methyl and all methylene signals occurred. This was the result of fluxional shifts of the Re moiety between the N/O donor pairs and rotation of the NEt$_2$ group on the pendant side of the ligand. The relatively slow rates of magnetisation transfer arising from these processes were measured by 2D-EXSY as well as by 1D-bandshape analysis. The 2D-EXSY spectrum of [ReBr(CO)$_3$tepdc] at 343 K is shown in Figure 3.

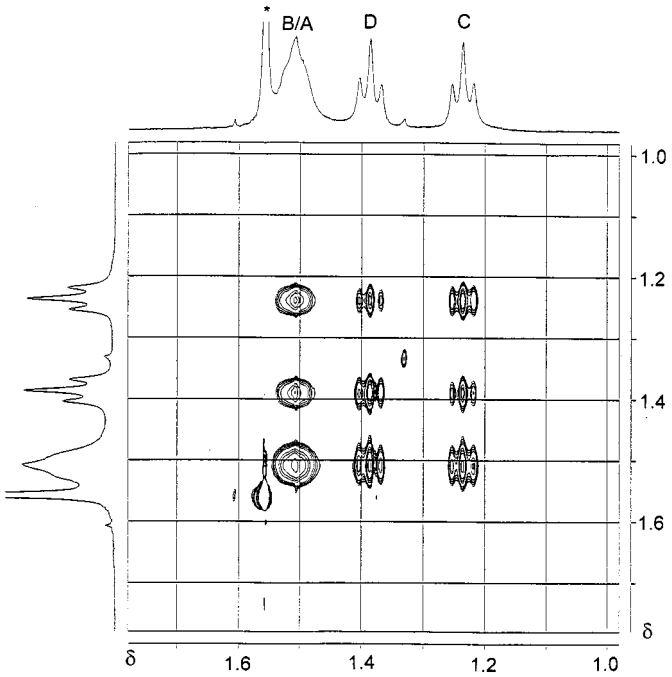


Figure 3. 400 MHz ^{1}H 2D-EXSY spectrum of [ReBr(CO)$_3$tepdc] at 343 K in $(CDCl_2)_2$ solution. Mixing time was 0.4 s. Cross peaks indicate restricted rotation in the pendant −C(O)NEt$_2$ group and 1,4-metallotropic shifts

At this temperature the methyl signals of the coordinated carboxamide moiety have coalesced, and cross peaks are observed between all three methyl signals. Cross peaks between the two lowest frequency signals (C and D) associated with the pendant carboxamide moiety, were due to restricted C−N rotation in this moiety, whereas the cross peaks between the signals C and D and the coalesced signal B/A was due to the metallotropic shift.

Table 5. Activation energy data for $C-NR_2$ restricted rotation in the pyridine-carboxamide and -thioamide ligands

Ligand	Temp range/K	Method[a]	$\Delta H^{\neq}$ /kJ mol^{-1}	$\Delta S^{\neq}$ /J K^{-1} mol^{-1}	$\Delta G^{\neq}$ [b] /kJ mol^{-1}
dmpc	323−373	BSA	81.2 ± 2.2	19.8 ± 6.7	75.3 ± 0.3[c]
tmpdc	333−373	BSA	72.7 ± 1.5	-7.3 ± 4.2	74.9 ± 0.2[d]
tepdc	333−383	BSA	108.5 ± 3.9	96.6 ± 6.6	79.8 ± 0.7
dmpt	353−393	EXSY	86.3 ± 0.2	-7.2 ± 0.5	88.4 ± 0.03
tmpdt	353−393	EXSY	107.8 ± 9.4	49.3 ± 25.3	93.2 ± 1.9
tepdt	353−393	EXSY	87.1 ± 0.5	-2.9 ± 1.3	88.0 ± 0.1

[a] BSA -^{1}H bandshape analysis, EXSY - ^{1}H exchange spectroscopy. − [b] At 298.15 K. − [c] Ref.[12] gives 74.9 kJ mol^{-1} (BSA); Ref.[16] gives 73.4 kJ mol^{-1} (coalescence 361 K).

Rate data for the restricted C−N rotation of the pendant -C(O)NEt$_2$ group (k_{RRP}) were obtained from the 2D-EXSY spectrum at 343 K and from the 1D spectra at 343, 353 and 363 K.

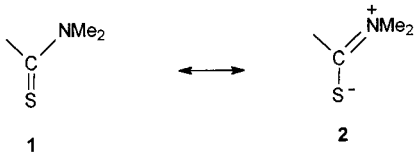
Rate constants for the metallotropic shifts (k_{MS}) were most accurately extracted from the 1D spectra of the pyridyl hydrogens, since this process interconverts the hydrogen atoms at the 3- and 5-position, but leaves that at the 4-position unaffected. Bandshape analysis of seven spectra in the temperature range 293−353 K provided reliable rate data for this fluxional process.

Discussion

Activation energy data for $C-NR_2$ restricted rotation in all six free ligands are collected in Table 5. Gibbs free energy values, $\Delta G^{\neq}$ (298.15 K), have the lowest associated uncertainties and it is most meaningful to make comparisons with this parameter. The 2-pyridine-carboxamide and 2,6-pyridine dicarboxamide, dmpc and tmpdc, have been studied previously, albeit rather less accurately in one case, and the present $\Delta G^{\neq}$ values of 75.3 and 74.9 kJ mol^{-1} are in moderately good agreement with the previous values of 74.9[12] and 73.4[16] kJ mol^{-1}.

These results imply that there is negligible electronic influence between the two amide groups in these systems. Replacement of the NMe_2 groups by NEt_2 appears to cause a slight rise in the C−N rotational barrier with the value for tepdc being 79.8 kJ mol^{-1}.

Replacement of the carbonyl oxygen of the amides by a sulfur atom in the thioamides causes a very significant increase in the C−N rotation barrier as can be seen by comparing $\Delta G^{\neq}$ data for the ligand pairs dmpc/dmpt, tmpdc/tmpdt and tepdc/tepdt, where increases of 13.1, 18.3 and 8.2 kJ mol^{-1}, respectively, occur. These increases are of similar magnitude to the increase of 9.6 kJ mol^{-1} which occurs on going from *N*,*N*-dimethylbenzamide[17] to the corresponding thioamide.[18] These increases may be attributed primarily to increased conjugation of the C−N bond(s) with the aromatic rings in the thioamide systems relative to the carboxamide systems, or alternatively to an increased contribution of the resonance form **2** below.



1 **2**

Such rationalisation is supported by the observation that in nonaromatic analogues such as *N*,*N*-dimethylcarbamoyl chloride $ClC(O)NMe_2$, and its thiocarbamoyl analogue $ClC(S)NMe_2$, the increase in the rotation energy barrier is only 5.4 kJ mol^{-1}.[19] However, recent ab initio calculations on formamide/thioformamide[20] and acetamide/thioacetamide[21] systems have implied that conjugation effects may not be the dominant contributors to C−N rotational barriers, but that the nitrogen lone pair may play a crucial role. For instance, a valence-bond study[20] suggests that the preferred orientation of the N lone pair perpendicular to the molecular plane may lead to resonance stabilisation of planar conformers which is responsible for about one half of the rotational barrier of formamide and two thirds of the barrier for thioformamide, the large magnitude of the latter being due to greater conjugation effects. An MO study[21] of acetamide and thioacetamide ascribes even greater importance to the N lone pair and the preference of the N atom for pyramidalization.

The full set of activation energy data for the various motional processes occurring in the $[ReX(CO)_3L]$ (X = Cl, Br) complexes is listed in Table 6.

For the complexes where L = tmpdc, tepdc and tmpdt, there appears to be no significant changes in the $\Delta G^{\neq}$ data for a change of halogen. The effect of Re coordination of the ligand on the C−N rotational characteristics of the $-C(E)NR_2$ groups is, however, particularly significant. This is highlighted in Table 7 where $\Delta G^{\neq}$ values for this process in both the coordinated and pendant portions of the complex are compared with the values for the free ligand.

Rhenium coordination of the amide oxygen reduces the -$C-NR_2$ rotation barriers by 2−13 kJ mol^{-1}, whereas coordination of the sulfur atom in the thioamide moieties greatly reduces the barrier by 28−33 kJ mol^{-1}. Metal σ-coordination acts as an electron drain on the carboxamide or thioamide functions, which will destabilise the zwit-

Table 6. Activation energy data for restricted C−NR_2 rotations and metallotropic shifts in [$ReX(CO)_3L$] (L = amide and thioamide ligands)

X	L	Temperature range /K	Motional process[a]	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	$\Delta G^{\ddagger}$/kJ mol^{-1}
Br	dmpc	313−373	RRC	80.2 ± 1.1	23.5 ± 3.1	73.2 ± 0.1
Br	dmpt	253−268	RRC	71.1 ± 3.6	34.3 ± 13.5	60.9 ± 0.5
Cl	tmpdc	303−353	RRC	66.9 ± 0.4	-10.9 ± 1.2	70.14 ± 0.03
		383−403	RRP	85.7 ± 1.3	-11.8 ± 3.3	89.2 ± 0.3
		343−413	MS	70.1 ± 3.7	-27.3 ± 10.0	78.3 ± 0.8
Br	tmpdc	313−353	RRC	61.4 ± 2.1	-26.3 ± 6.4	69.2 ± 0.2
		323−353	RRP	66.7 ± 9.2	-38.1 ± 27.1	78.0 ± 1.1
		343−413	MS	89.5 ± 1.6	19.2 ± 4.2	83.8 ± 0.4
Cl	tmpdt	263−333	RRC	70.1 ± 3.0	23.9 ± 10.3	62.93 ± 0.04
		383−413	RRP	92.7 ± 3.8	0.8 ± 9.6	92.4 ± 0.9
		383−413	MS	92.5 ± 2.5	14.6 ± 6.3	88.1 ± 0.6
Br	tmpdt	263−313	RRC	66.6 ± 1.07	20.9 ± 3.7	60.38 ± 0.02
		383−413	RRP	85.7 ± 9.3	-22.5 ± 23.3	92.4 ± 2.3
		383−413	MS	93.7 ± 1.4	14.9 ± 3.5	89.2 ± 0.3
Cl	tepdc	293−353	RRC	69.9 ± 1.7	8.9 ± 5.3	67.2 ± 0.1
		343−413	MS	73.5 ± 0.4	-13.4 ± 1.1	77.5 ± 0.1
Br	tepdc	293−353	RRC	71.4 ± 1.5	13.8 ± 3.2	67.3 ± 0.1
		343[b]	RRP	-	-	84.1
		343−363	RRP	78.9 ± 5.0	-0.2 ± 14.2	79.0 ± 0.8
		343−413	MS	78.2 ± 1.2	-1.7 ± 3.2	78.8 ± 0.3

[a] RRC = *r*estricted *r*otation on *c*oordinated side; RRP = *r*estricted *r*otation on *p*endant side; MS = *m*etallotropic *s*hift. − [b] 2D-EXSY value.

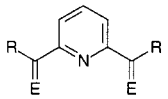
Table 7. Comparison of energy barriers for restricted C−N rotations for coordinated and uncoordinated amides −C(E)NR_2

Ligand, L	E	$\Delta G^{\ddagger}$/ (298.15 K)/kJ mol^{-1} Free ligand	[$ReBr(CO)_3L$]	$\Delta\Delta G^{\ddagger}$ [a]/ kJ mol^{-1}
dmpc	O	75.3	73.2 (coord)	−2.1
dmpt	S	88.4	60.9 (coord)	−27.5
tmpdc	O/O	74.9	69.2 (coord)	−5.7
			78.0 (pendant)	3.1
tepdc	O/O	79.8	67.3 (coord)	−12.5
			84.1 (pendant)	4.3
tmpdt	S/S	93.2	60.4 (coord)	−32.8
			92.4 (pendant)	−0.8

[a] $\Delta G^{\ddagger}$ (complex) − $\Delta G^{\ddagger}$ (free ligand).

Table 8. Activation energies of metallotropic shifts in [$ReBr(CO)_3L$] complexes

L =



R	E	$\Delta G^{\ddagger}$(298.15 K)/kJ mol^{-1}	Reference
Me_2N	O	83.8 ± 0.4	This work
Et_2N	O	78.8 ± 0.3	This work
Me_2N	S	89.2 ± 0.3	This work
Me	O	61.0 ± 0.05	[22]
H	O	Low[a]	[23]
^{t}Bu	O	63.5 ± 0.1	[23]
OMe	O	60.0 ± 0.1	[23]
OEt	O	60.3 ± 0.1	[23]

[a] Not measurable, complex thermally unstable.

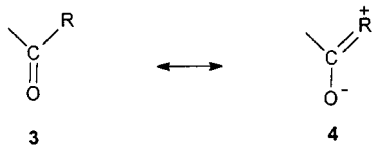
terionic form of the function leading to a decrease in the energy barrier to C−N rotation. This effect appears to be much stronger for the sulfur atom with its greater *p* electron complement compared to oxygen. Not unexpectedly, the barriers for the pendant portions of the ligands in the complex are of similar magnitude to those of the free ligand. For O coordination there is a small increase of 3−4 kJ mol^{-1} in the complex, and for S coordination there is a slight decrease of 0.8 kJ mol^{-1}.

Metallotropic shifts involving interchange of bidentate, chelate bonding between adjacent donor pairs in N_3 ligands have been reported for a variety of metal moieties, but data for the moiety $ReX(CO)_3$ where X is halogen, are most widely available. Much fewer data are available for metallotropic shifts in O, N, O and S, N, S ligands. However, Table 8 contains the activation energies [$\Delta G^{\ddagger}$ (298.15 K)] for a variety of complexes of general type [$ReBr(CO)_3L$] (L = 2,6-disubstituted pyridines where the substituents are either amides, thioamides, ketones or esters) from both published and unpublished work. $\Delta G^{\ddagger}$ values lie in the range 60−89 kJ mol^{-1}.

An increase in magnitude of ca. 5 kJ mol^{-1} on changing from a dicarboxamide to a dithioamide ligand mirrors somewhat the relative energies of C−N rotation of the analogous free ligands, and can again be related to increased conjugation of the -C=S function as opposed to the -C=O function with the pyridyl aromatic ring, thus increasing the donor strength of the S atoms.

Energy barriers for the -C(O)R groups also vary appreciably with the nature of R, being in the range 60−84 kJ mol^{-1}. The highest values, 79−84 kJ mol^{-1}, are associated with the strong electron donors NMe_2, NEt_2, and lower values, in the range 60−64 kJ mol^{-1}, with the weaker electron donors OMe, OEt, Me and *t*Bu. This can be rationalised in terms of the strength of the oxygen donor being increased by the extent to which its electron density is enhanced by donation from the R group, i.e. the extent to

which resonance form **4** (below) contributes to the overall structure.



3 **4**

The mechanism of 1,4 metallotropic shifts has been the subject of some controversy as to whether it has a dissociative or associative mechanism.[3] The present study does not provide further insight into this matter as no investigation was made into whether the rearrangement interchanged the equatorial carbonyl environments or not. This would have required variable temperature ^{13}C studies of the type performed on the E = O; R = Me complex.[22] This earlier study showed exchange broadening of the equatorial CO environments accompanying the metal fluxion, which lent support to an associative mechanism involving pairwise breaking and making of both metal coordinate bonds in a "windscreen wiper" or "tick-tock twist" process.[3] It would be surprising if the same mechanism was not operating in the present complexes

Experimental Section

Materials: The carboxamide ligands, *N*,*N*-dimethyl-2-pyridinecarboxamide (dmpc), *N*,*N*,*N*′,*N*′-tetramethyl-2,6-pyridinedicarboxamide (tmpdc) and *N*,*N*,*N*′,*N*′-tetraethyl-2,6-pyridinedicarboxamide (tepdc) were prepared by adapting literature methods.[8][24] The thioamides *N*,*N*-dimethyl-2-pyridinethioamide (dmpt), *N*,*N*,*N*′,*N*′-tetramethyl-2,6-pyridinedithioamide (tmpdt) and *N*,*N*,*N*′,*N*′-tetraethyl-2,6-pyridinedithioamide (tepdt) were prepared by treating the corresponding carboxamide with Lawesson′s reagent.[25]

Measurements: Elemental analyses were carried out by Butterworth Laboratories Ltd., Teddington, Middlesex, UK. − Melting temperatures were recorded on a Gallenkamp apparatus and are uncorrected. Infrared spectra were measured with a Nicolet Magna FT-IR instrument. − ^1H NMR spectra were recorded on a Bruker DRX400 instrument operating at 400.13 MHz. A standard B-VT2000 variable temperature unit was used to control the probe temperature, the calibration of this unit being checked periodically against a Comark digital thermometer. The temperatures are considered to be accurate to ±1 °C. Rate data were derived from band-shape analysis of the ^1H spectra using a version of the DNMR3 program,[26] or from 2D-EXSY spectra using volume integration data in the authors D2DNMR program.[27] − Activation parameters based on experimental rate data were calculated using the THERMO program.[28] − Two-dimensional exchange (EXSY) spectra were obtained using the standard Bruker program NOESY-PH.AU.

Synthesis of Complexes: All preparations were carried out using standard Schlenk techniques under purified nitrogen using freshly distilled and degassed solvents. Synthetic and analytical data are given in Table 1. The preparation of the complex [$ReBr(CO)_3$(dmpc)] is described by way of illustration.

Bromotricarbonyl(*N*,*N*-dimethyl-2-pyridinecarboxamide)rhenium(I): The compounds [$ReBr(CO)_5$] (0.23 g, 0.57 mmol) and dmpc (0.1 g, 0.67 mmol) were dissolved in benzene (15 cm^3) with gentle warming to produce a colourless solution. The solution was heated under reflux for 4 h and then hexane (20 cm^3) was added to the hot solution. After allowing the solution to stand at ambient temperature for 9 h the solvent was decanted off and the yellow solid washed with hexane (3 × 20 cm^3). The sample was then dried in vacuum for 7 h. Yield 0.27 g (93%).

Acknowledgments

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