DALTON

Synthesis and solution fluxionality of rhenium(I) carbonyl complexes of 2,4,6-tris(pyrazolyl)pyrimidines (L), $[ReX(CO)_3L]$ (X = Cl, Br or I). Isolation and identification of the dinuclear complex $[\{ReBr(CO)_3\}_2L]$

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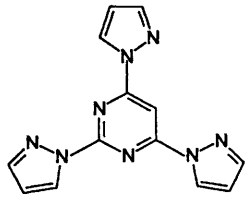
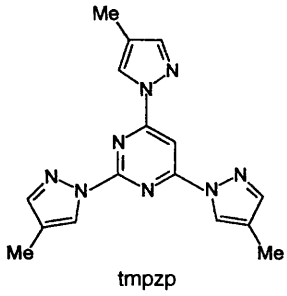
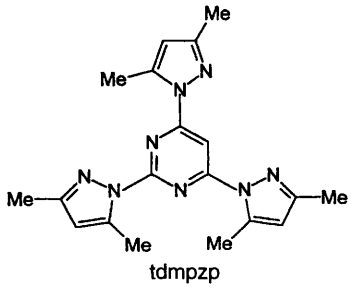
2,4,6-Tris(pyrazolyl)pyrimidines reacted with pentacarbonylhalogenorhenium(I) complexes to form stable mixtures of bidentate, chelate complexes of types *fac*-$[ReBr(CO)_3(tpzp)]$, *fac*-$[ReBr(CO)_3(tmpzp)]$ and *fac*-$[ReX(CO)_3(tdmpzp)]$ (X = Cl, Br or I) where tpzp = 2,4,6-tris(pyrazol-1-yl)pyrimidine, tmpzp = 2,4,6-tris(4-methylpyrazol-1-yl)pyrimidine and tdmpzp = 2,4,6-tris(3,5-dimethylpyrazol-1-yl)pyrimidine. In solution the complexes involving co-ordination with the 2-pyrazolyl ring nitrogen rather than the 4- or 6-pyrazolyl ring nitrogens strongly predominated (> 91%). Fluxional exchange between the two types of co-ordination species of tmpzp and tdmpzp was detected and measured quantitatively by dynamic NMR methods. Activation energies $\Delta G^{\ddagger}$ (298 K) for the fluxions were in the range 53–74 kJ mol^{-1}. Dinuclear transition-metal complexes of type $[\{ReBr(CO)_3\}_2L]$ (L = tmpzp or tdmpzp) were also isolated. Structures were attributed to these non-fluxional complexes in solution.

Recent work by us[1–7] and others[8] has established the widespread existence of 1,4-metallotropic shifts in bidentate, chelate transition-metal complexes of three-ring N-heterocyclic ligands. Compounds such as 2,2′:6′,2″-terpyridine (terpy), 2,6-bis(pyrazol-1-yl)pyridine (bppy), and 6-(pyrazol-1-yl)-2,2′-bipyridine (pbipy) utilize only two of their three nitrogen donors in forming bidentate, chelate complexes with metal moieties of facial geometry, *viz.* $PtXMe_3$ or $ReX(CO)_3$. However, these complexes undergo 1,4-metallotropic shifts in solution whereby involvement of the third nitrogen donor in co-ordination is achieved. The exchanging pair of co-ordination species may be chemically identical (*e.g.* terpy or bppy)[1–6,8] or different (*e.g.* pbipy)[7] according to the symmetry of the ligand, and the fluxion proceeds intramolecularly *via* a 'tick-tock' twist mechanism.

We now wish to examine the nature of metal complexes of ligands with the potential for exhibiting fluxionality at more than one metal centre. Such complexes are readily formed with ligands in which the central ring acts as a branching centre to other groups. There is much flexibility in the choice of both branching centres (*e.g.* benzene, 1,3-pyrimidine, 1,3,5-triazine) and peripheral groups (*e.g.* pyridine, pyrazole, bipyridine or terpyridine). The ligand, however, must contain at least five nitrogen donor atoms, composed of sets of three donors that are capable of terdentate chelate bonding to a metal, if there is to be potential fluxionality of two metal centres. This work discusses complexes based on such ligands where the branching centre is pyrimidine and the peripheral rings are pyrazoles. Such ligands can form both 1:1 and 2:1 metal:ligand complexes with moieties such as $M(CO)_4$ and $MX(CO)_3$. We report here on solution NMR studies of the 1:1 complexes *fac*-$[ReX(CO)_3L]$ [X = Br, L = 2,4,6-tris(pyrazol-1-yl)pyrimidine (tpzp) or 2,4,6-tris(4-methylpyrazol-1-yl)pyrimidine (tmpzp); X = Cl, Br or I, L = 2,4,6-tris(3,5-dimethylpyrazol-1-yl)pyrimidine (tdmpzp)] and of the 2:1 complexes $[\{ReBr(CO)_3\}_2(tmpzp)]$ and $[\{ReBr(CO)_3\}_2(tdmpzp)]$.







Experimental

Materials

The complexes $[ReX(CO)_5]$ (X = Cl, Br or I) were prepared using previously described methods.[9,10] 4-Methylpyrazole was obtained from Janssen Chimica and used without further purification. Pyrazole, 3,5-dimethylpyrazole and 2,4,6-trichloropyrimidine were obtained from Aldrich and used without further purification.

Synthesis of tris(pyrazolyl)pyrimidines

2,4,6-Tris(pyrazol-1-yl)- and 2,4,6-tris(4-methylpyrazol-1-yl)-pyrimidine were prepared by the reaction of 2,4,6-trichloro-

pyrimidine with the potassium salt of the corresponding pyrazole. 2,4,6-Tris(3,5-dimethylpyrazol-1-yl)pyrimidine was prepared in an analogous manner and is described below in more detail.

2,4,6-Tris(3,5-dimethylpyrazol-1-yl)pyrimidine. 2,4,6-Trichloropyrimidine (2.0 g, 10.90 mmol) was added to 3 molar equivalents of potassium 3,5-dimethylpyrazolate [prepared from equimolar quantities of 3,5-dimethylpyrazole and potassium metal at 70 °C in anhydrous diglyme (2,5,8-trioxanonane) (50 cm^3)] and the resultant mixture was stirred at 135 °C for 5 d. The solvent was removed *in vacuo* and the resulting yellow solid dissolved in 1 mol dm^3 hydrochloric acid (30 cm^3); the solution was then made neutral by addition of dilute aqueous sodium hydroxide. Extraction with dichloromethane (3 × 200 cm^3) followed by drying over $MgSO_4$ and removal of the solvent yielded a pale yellow oily solid. This was washed with hexane (50 cm^3) to give the product as a white solid (2.25 g) in 57% yield.

Synthesis of complexes

All preparations were carried out using standard Schlenk techniques[11] under purified nitrogen using freshly distilled and degassed solvents.

1:1 Complexes. The complexes $[ReX(CO)_3L]$ (L = tpzp, tmpzp, X = Br; L = tdmpzp, X = Cl, Br or I) were all prepared in a similar manner. Details for $[ReI(CO)_3(tdmpzp)]$ are given below. Synthetic, analytical and mass spectral data are given in Tables 1 and 2.

Tricarbonyliodo[2,4,6-*tris*(3,5-*dimethylpyrazol*-1-*yl*)*pyrimidine*]*rhenium*(I). The compound $[ReI(CO)_5]$ (0.23 g, 0.51 mmol) and tdmpzp (0.2 g, 0.55 mmol) were dissolved in benzene (60 cm^3) and the mixture heated under reflux for 14 h, after which time the solution infrared spectrum showed the absence of signals at 2145, 2041 and 1986 cm^{-1}, indicating loss of $[ReI(CO)_5]$. The volume was reduced to *ca.* 20 cm^3 and light petroleum (b.p. 40–60 °C, 100 cm^3) added to precipitate a yellow solid. The almost colourless solvent was decanted and the solid dried under vacuum. Recrystallization from dichloromethane–hexane gave the desired product as orange crystals (0.28 g). Yield 67%.

2:1 Complexes. The complexes $[\{ReBr(CO)_3\}_2L]$ (L = tmpzp or tdmpzp) were prepared in a similar manner by two different routes. The first was the same as that described above for the 1:1 complexes but using twice as much $[ReBr(CO)_5]$. The solution was again refluxed until the infrared spectrum showed the absence of the signals due to $[ReBr(CO)_5]$ (≈36 h). After this time the product, which was much less soluble than the corresponding 1:1 complex, had begun to precipitate. Work-up as before yielded the desired product as orange crystals. Yield 55–65%.

The second synthetic route involved treating $[ReBr(CO)_5]$ with $[ReBr(CO)_3L]$ under analogous conditions to those described above. Yields for the two routes were not significantly different. Synthetic and analytical data are given in Table 1.

Physical methods

Hydrogen-1 NMR spectra were recorded on either Bruker AC-300 or DRX-400 spectrometers operating at 300.13 or 400.13 MHz respectively. All spectra were recorded in $CDCl_3$, CD_2Cl_2 or $CDCl_2CDCl_2$ solutions. Standard B-VT 1000 variable-temperature units were used to control the probe temperature, their calibration being checked periodically against a Comark digital thermometer. Sample temperatures are considered accurate to ± 1 °C. A mixing time of 0.1 s was used for the two-dimensional exchange (EXSY) spectra of the complex $[ReBr(CO)_3(tdmpzp)]$ using the standard Bruker NOESYPH.AU program. Rate data were based on bandshape analysis of ^1H spectra using the authors' version of the standard DNMR 3 program.[12] Activation parameters based on experimental rate data were calculated using the THERMO program.[13] Infrared spectra were recorded on a Perkin-Elmer 881 spectrometer calibrated from the signal of polystyrene at 1602 cm^{-1}. Electron-impact mass spectra were obtained on a Kratos Profile spectrometer. Elemental analyses were performed by Butterworth Laboratories, Teddington, Middlesex, London.

Results

The metal complexes were characterized by their IR, elemental analysis and mass spectral data (Tables 1 and 2), the proligands by their ^1H NMR data (Table 3). The symmetry of the latter compounds causes chemical equivalence of the pyrazolyl rings attached to the 4 and 6 positions of the pyrimidine ring [*i.e.* corresponding signals in the groups labelled D–F and G–I (Table 3) are identical], causing the signals A–C and D–I to be in an intensity ratio of 1:2. Metal co-ordination removes this symmetry element and renders all ring hydrogen environments different. Thus, ten distinct chemical shifts occur for each of the bidentate chelate complexes of tmpzp and tdmpzp (Tables 4 and 5).

At the outset of this work it was expected that comparable amounts of both possible tricarbonylrhenium(I) halide complexes would be formed, in view of the almost identical nature of the chelate rings associated with either form. However, solution NMR studies indicated a very strong imbalance between the two types of complexes (shown in Tables 4 and 5), the population ratio being greater than 90:10 for all the tmpzp and tdmpzp complexes. The most likely explanation for this lies in the difference in preferred conformations of the free and co-ordinated tris(pyrazolyl)pyrimidines.

In 2,6-bis(pyrazol-1-yl)pyridine (bppy) the full structure is essentially planar with the pyrazole rings adopting a configuration whereby their N heteroatoms are *trans* with respect to the pyridyl N atom. Such a structure occurs exclusively in the solid state[14] and is strongly preferred in solution.[5] By analogy, the preferred conformations of tpzp, tmpzp and tdmpzp are those shown at the head of Table 3. Here it should be noted that the N heteroatom of the 2-pyrazolyl ring is necessarily *cis* to one of the pyrimidine nitrogens and thus *ideally placed* to form a bidentate chelate complex. In contrast, the other two pyrazolyl rings need to rotate by 180° from their preferred pro-ligand *trans* conformations in order to be suitably placed for metal chelation. This would therefore account for co-ordination involving the 2-position pyrazolyl ring being much more strongly preferred to that involving the 4- and 6-pyrazolyl rings.

$[ReBr(CO)_3(tmpzp)]$

The chemical shift data for both the major and minor population forms of this complex were measured at a temperature of 203 K and are given in Table 4. The assignments of the major signals are definitive. However, only five out of the ten expected signals for the less-favoured complex were detected, the others presumably overlapping the signals of the major form. It was estimated from integration measurements that the population ratio of the major:minor species was *ca.* 24:1.

On warming the CD_2Cl_2 solution of the complex from 203 K the minor signals commenced broadening, becoming almost invisibly broad as a result of exchange with their major signal counterparts, *viz.* A ⇌ K, C ⇌ M, G ⇌ Q and I ⇌ S. It was estimated that these pairs of signals coalesced at 243 K, as maximum broadening of the major signals A, C, G and

Table 1 Synthetic and analytical data for the complexes $[ReX(CO)_3L]$ (X = Br, L = tpzp or tmpzp; X = Cl, Br or I, L = tdmpzp) and $[\{ReX(CO)_3\}_2L]$ (X = Br, L = tmpzp or tdmpzp)

			Analysis[c] (%)		
Complex	Yield[a] (%)	$\tilde{\nu}_{CO}$[b]/cm^{-1}	C	H	N
$[ReBr(CO)_3(tpzp)]$	65	2029.0s, 1925.0s, 1901.0s[d]	30.65 (30.55)	1.60 (1.60)	16.65 (17.85)
$[ReBr(CO)_3(tmpzp)]$	72	2031.0s, 1930.0s, 1902.0s	33.80 (34.05)	2.05 (2.40)	15.90 (16.70)
$[ReCl(CO)_3(tdmpzp)]$	57	2027.0s, 1923.0s, 1898.0s	39.15 (39.55)	3.00 (3.30)	16.15 (16.80)
$[ReBr(CO)_3(tdmpzp)]$	48	2027.0s, 1924.0s, 1899.0s	36.90 (37.10)	3.30 (3.10)	14.45 (15.75)
$[ReI(CO)_3(tdmpzp)]$	67	2027.0s, 1928.0s, 1904.0s	34.10 (34.80)	2.50 (2.90)	13.65 (14.75)
$[\{ReBr(CO)_3\}_2(tmpzp)]$	63	2031.0s, 2025.0sh, 1926.0s, 1902.0s	25.85 (25.90)	1.60 (1.55)	10.25 (11.00)
$[\{ReBr(CO)_3\}_2(tdmpzp)]$	55	2029.0s, 2022.0sh, 1919.0m, 1896.0m	27.65 (28.30)	2.05 (2.10)	8.60 (10.6)

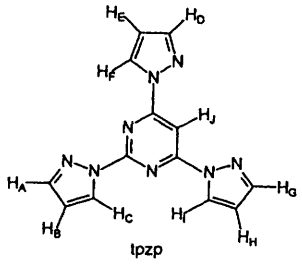
[a] Relative to the metal-containing reactant. [b] Recorded in benzene, s = strong. [c] Calculated values in parentheses. [d] Recorded in acetone.

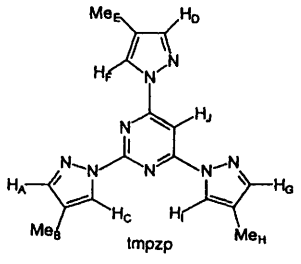
Table 2 Mass spectral data for the complexes $[ReX(CO)_3L]$ (X = Br, L = tpzp or tmpzp; X = Cl, Br or I, L = tdmpzp)

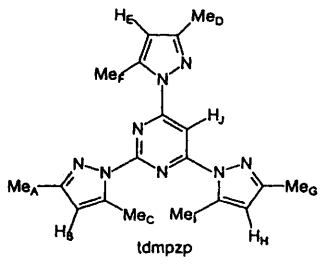
	m/z					
Complex	M^+	$[M - CO]^+$ *	$[M - 2CO]^+$	$[M - 3CO]^+$ *	$[M - 3CO - X]^+$	$[L]^+$
$[ReBr(CO)_3(tpzp)]$	628	600	572	544	464	278
$[ReBr(CO)_3(tmpzp)]$	670	642	614	586	506	320
$[ReCl(CO)_3(tdmpzp)]$	668	640	612	584	548	362
$[ReBr(CO)_3(tdmpzp)]$	712	684	656	628	548	362
$[ReI(CO)_3(tdmpzp)]$	760	732	704	676	548	362

* Dominant peak.

Table 3 Hydrogen-1 NMR data * for the tris(pyrazolyl)pyrimidines in $CDCl_3$ at 303 K







Compound	δ_A	δ_B	δ_C	δ_D	δ_E	δ_F	δ_G	δ_H	δ_I	δ_J
tpzp	7.84	6.49	8.59	7.79	6.49	8.66	7.79	6.49	8.66	8.33
tmpzp	7.64	2.15	8.32	7.59	2.13	8.38	7.59	2.13	8.38	8.14
tdmpzp	2.31	6.03	2.62	2.29	6.01	2.54	2.29	6.01	2.54	8.24

	$J(H_AH_B)$	$J(H_AH_C)$	$J(H_BH_C)$	$J(H_DH_E)$	$J(H_DH_F)$	$J(H_EH_F)$	$J(H_GH_H)$	$J(H_GH_I)$	$J(H_HH_I)$
tpzp	1.49	0.64	2.74	1.52	0.52	2.76	1.52	0.52	2.76
tmpzp	≈0	≈0	0.92	≈0	≈0	0.92	≈0	≈0	0.92
tdmpzp	≈0	≈0	≈0	≈0	≈0	≈0	≈0	≈0	≈0

* Chemical shifts, δ, relative to $SiMe_4$ (δ 0); spin–spin couplings constants, *J*, in Hz.

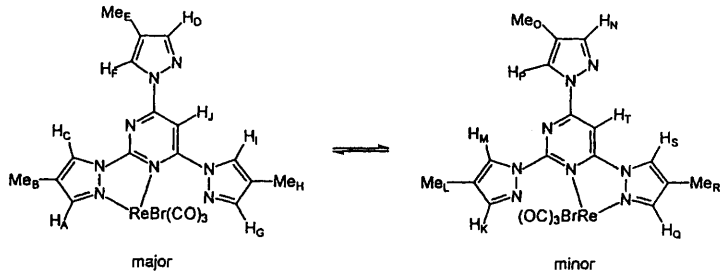
I was observed at this temperature. The bandshapes for these signals could be accurately simulated for an exchange rate constant of 23.0 s^{-1}, and a population ratio for the two fluxional species of 95.7:4.3. This enabled an estimate of $\Delta G^{\ddagger}$ for the fluxional process from the major to minor species to be calculated (Table 6).

$[ReX(CO)_3(tdmpzp)]$ (X = Cl, Br or I)

Chemical shift data for all three complexes are collected in Table 5. There is relatively little halogen dependence of the shifts. In all cases there are significant positive internal co-ordination shifts, Δδ, for the hydrogen pairs A/K, B/L and C/M, and appreciable negative shifts for the pairs G/Q, H/R, I/S and J/T (N.B. All values of Δδ refer to the differences major – minor signals, and not the reverse). Unsurprisingly, the hydrogens associated with the pyrazolyl ring which is *not* involved in the metal co-ordination exhibit vanishingly small internal co-ordination shifts.

On warming solutions of these three complexes from 273 K their ^1H NMR spectra show changes which reflect the onset of switching of the $ReX(CO)_3$ moiety between two of the three pyrazolyl rings. Signals due to hydrogens on the third pyrazolyl ring (*viz.* hydrogens D–F and N–P) show little change. It was decided to monitor the fluxion by its effects on the methyl signals of the two complexes. There are twelve such signals, an intense set, labelled A, C, D, F, G and I, due to the major co-ordination species, and a weak set, labelled K, M, N, P, Q and S, due to the low-population co-ordination complex. In order to identify the six exchanging pairs a ^1H two-dimensional EXSY spectrum of $[ReBr(CO)_3(tdmpzp)]$ in $CDCl_2CDCl_2$ at 296 K was recorded (Fig. 1). It can be seen from this spectrum that exchange cross-peaks clearly identified the methyl exchanges A ⇌ K,C ⇌ M,F ⇌ P,G ⇌ QandI ⇌ S.Exchange between the methyls D and N, associated with the pyrazolyl ring *not* involved in the fluxion, could not be identified as these methyls were virtually isochronous. Instead of extracting rate data from this and other two-dimensional EXSY spectra at

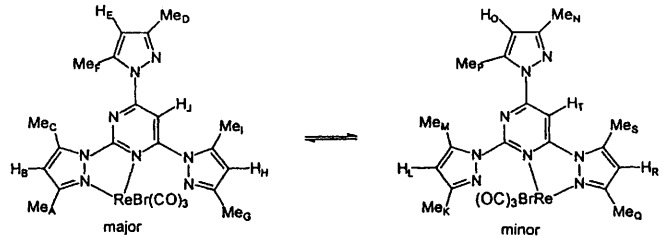
Table 4 Hydrogen-1 NMR chemical shift data[a] for the complex [ReBr(CO)$_3$(tmpzp)] in CD_2Cl_2 at 203 K



	δ									
	H_A/H_K	H_B/H_L	H_C/H_M	H_D/H_N	H_E/H_O	H_F/H_P	H_G/H_Q	H_H/H_R	H_I/H_S	H_J/H_T
	8.01 (H_A)	2.18 (H_B)	8.47 (H_C)	7.76 (H_D)	2.15 (H_E)	8.34 (H_F)	7.79 (H_G)	2.16 (H_H)	8.10 (H_I)	7.77 (H_J)
	8.06 (H_K)	?	8.16 (H_M)	7.66 (H_N)	≈2.15 (H_O)	≈8.34 (H_P)	7.89 (H_Q)	≈2.16 (H_R)	8.28 (H_S)	?
$\Delta\delta^b$	−0.05	?	0.31	0.10	≈0	≈0	−0.10	≈0	−0.18	?

[a] Values relative to $SiMe_4$ (δ 0). [b] Internal co-ordination shifts, Δδ (= $\delta_{H_A} - \delta_{H_K}$, $\delta_{H_B} - \delta_{H_L}$, *etc.*).

Table 5 Hydrogen-1 NMR data[a] for the complexes [ReX(CO)$_3$(tdmpzp)] (X = Cl, Br or I) in $CDCl_2CDCl_2$



		δ									
X	*T*/K	H_A/H_K	H_B/H_L	H_C/H_M	H_D/H_N	H_E/H_O	H_F/H_P	H_G/H_Q	H_H/H_R	H_I/H_S	H_J/H_T
Cl	263	2.59 (H_A)	6.30 (H_B)	2.79 (H_C)	2.29 (H_D)	6.19 (H_E)	2.72 (H_F)	2.32 (H_G)	6.22 (H_H)	2.47 (H_I)	7.86 (H_J)
		2.31 (H_K)	6.16 (H_L)	2.56 (H_M)	≈2.29 (H_N)	≈6.19 (H_O)	2.68 (H_P)	2.60 (H_Q)	6.35 (H_R)	2.80 (H_S)	8.16 (H_T)
	$\Delta\delta^b$	0.28	0.14	0.23	≈0	≈0	0.04	−0.28	−0.13	−0.33	−0.30
Br	273	2.60 (H_A)	6.31 (H_B)	2.81 (H_C)	2.31 (H_D)	6.20 (H_E)	2.74 (H_F)	2.34 (H_G)	6.23 (H_H)	2.49 (H_I)	7.87 (H_J)
		2.33 (H_K)	6.16 (H_L)	2.57 (H_M)	2.31 (H_N)	≈6.20 (H_O)	≈2.69 (H_P)	2.62 (H_Q)	6.36 (H_R)	2.83 (H_S)	8.19 (H_T)
	Δδ	0.27	0.15	0.24	≈0	≈0	0.05	−0.28	−0.16	−0.34	−0.32
I	283	2.60 (H_A)	6.32 (H_B)	2.84 (H_C)	2.31 (H_D)	6.21 (H_E)	2.74 (H_F)	2.35 (H_G)	6.23 (H_H)	2.51 (H_I)	7.87 (H_J)
		2.34 (H_K)	6.18 (H_L)	2.57 (H_M)	≈2.31 (H_N)	≈6.21 (H_O)	2.69 (H_P)	2.62 (H_Q)	6.38 (H_R)	2.85 (H_S)	8.21 (H_T)
	Δδ	0.26	0.14	0.27	≈0	≈0	0.05	−0.27	−0.15	−0.34	−0.34

[a] Chemical shifts, δ, relative to $SiMe_4$ (δ 0). [b] Internal co-ordination shifts Δδ (= $\delta_{H_A} - \delta_{H_K}$, $\delta_{H_B} - \delta_{H_L}$, *etc.*).

Table 6 Activation-energy data[a] for the 1,4 Re–N fluxions in [ReX(CO)$_3$L] complexes

L	X	Population[b] (%)	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}	$\Delta G^‡$ (298.15 K)/kJ mol^{-1}
tmpzp	Br	95.7:4.3	*c*	*c*	52.8 ± 3.0[d]
tdmpzp	Cl	92.0:8.0	66.9 ± 1.2	2.5 ± 3.8	66.2 ± 0.1
	Br	91.6:8.4	68.2 ± 1.0	−17.8 ± 2.9	73.5 ± 0.1
	I	91.3:8.7	69.0 ± 1.6	−5.2 ± 4.6	71.0 ± 0.2
bmppy	Br	50:50	54.9 ± 0.9	0.5 ± 3.6	54.8 ± 0.1
bdtmppy	Br	50:50	68.5 ± 0.4	−15 ± 1	72.9 ± 0.1

[a] For major ⟶ minor co-ordination species. Errors are statistical, based on least-squares fittings of Eyring plots. [b] Values ±0.5%. [c] The $\Delta G^‡$ was based on an estimate from a coalescence temperature of 243 K and therefore no $\Delta H^‡$ or $\Delta S^‡$ values of any great reliability could be calculated. [d] Measured at 243 K only.

different temperatures it was decided that greater accuracy would be achieved by applying bandshape analysis to the two exchanging pairs of signals which showed the greatest amount of exchange broadening at higher temperatures, namely the pairs C ⇌ M and I ⇌ S. Variable-temperature spectra of these methyl signals (plus others) in the range 273–393 K for [ReBr(CO)$_3$(tdmpzp)] are shown in Fig. 2. Theoretical band shapes for the signal pairs C ⇌ M and I ⇌ S, based on the 'best-fit' rate constants, are also shown in the figure. From these rate data activation energies for the fluxional process were calculated in the usual way (Table 6). Similar band shape fittings were performed on the spectra of the other two halide complexes.

An examination of the energy data in Table 6 reveals certain consistent trends. In all cases, there is a strong preference in solution for the complex involving co-ordination with the pyrazolyl ring attached to the 2 position of the pyrimidine centre. A rationalization of this observation has been given (see above). Introduction of methyl groups to the 3 and 5 positions of the pyrazolyl rings (instead of to the 4 position) gives slightly

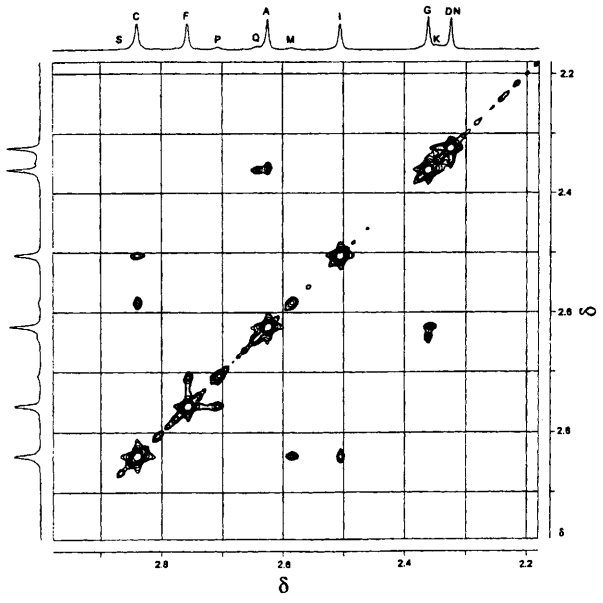


Fig. 1 A 400 MHz ^{1}H two-dimensional EXSY NMR spectrum (methyl signals only) of [ReBr(CO)$_3$(tdmpzp)] in $CDCl_2CDCl_2$ at 296 K. Mixing time 0.1 s. Signal labelling refers to Table 5

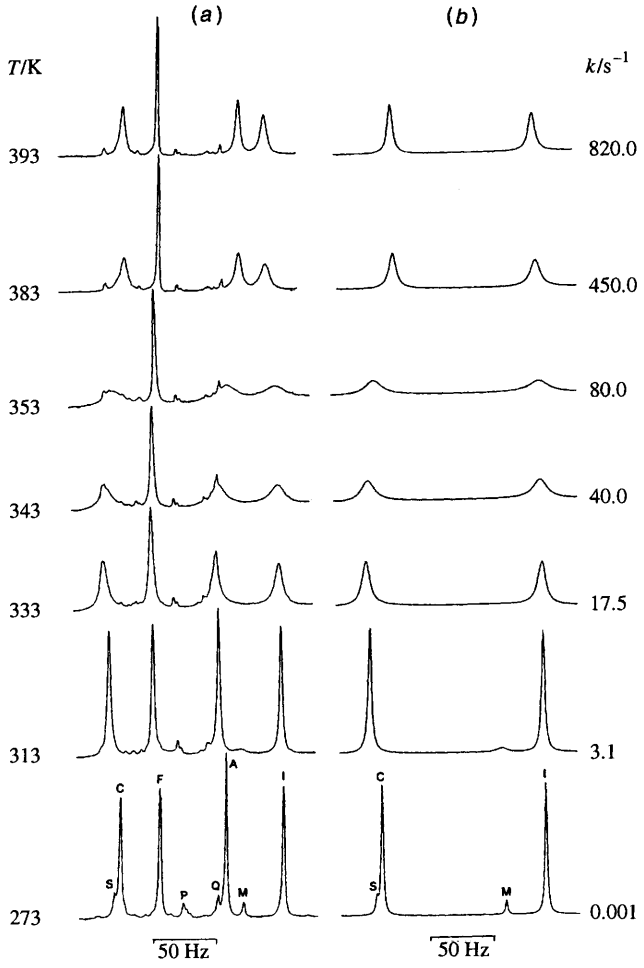
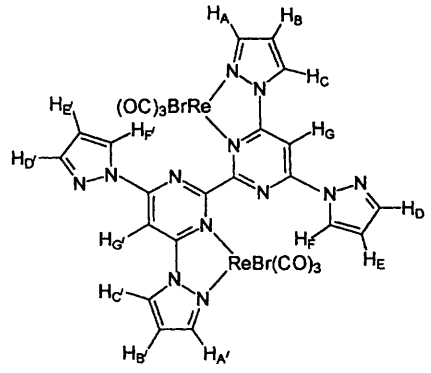


Fig. 2 The 300 MHz ^{1}H NMR spectra (portion of methyl region only) of [ReBr(CO)$_3$(tdmpzp)] in $CDCl_2CDCl_2$ in a temperature range 273–393 K (*a*). Computer-simulated spectra (*b*) of the exchanging pairs C/M and I/S are shown alongside for the best-fit rate constants at each temperature

lower preference to this 2-pyrazolyl co-ordinated complex although it is still very dominant. Whilst the effects of methyl substitution on the relative populations of the two co-ordinated species are slight, their effects on the rates and activation



energies of the 1,4-metallotropic shifts are substantial with activation energies (expressed as $\Delta G^{\ddagger}$ data) increasing by *ca.* 20 kJ mol^{-1}. This is very comparable to the analogous complexes of pyridine, namely 2,6-bis(4-methylpyrazol-1-yl)pyridine (bmppy)[6] and 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine (bdmppy)[5] where the difference in activation free energies is 18.1 kJ mol^{-1} (see Table 6). In these latter two complexes it should be noted that both co-ordination species are chemically identical and so the solution population ratios are 1:1.

[ReBr(CO)$_3$(tpzp)]

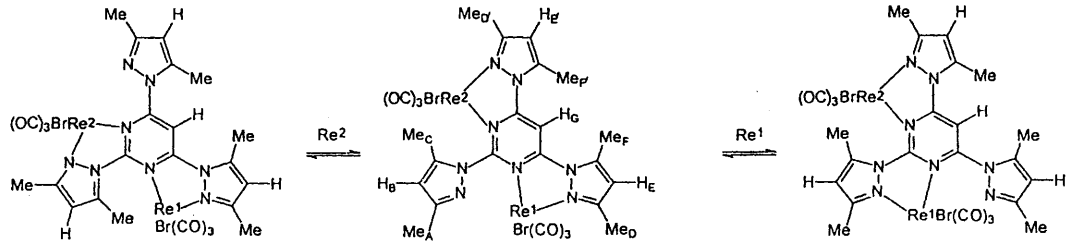
This complex, consisting of unsubstituted pyrazolyl rings, proved to be highly insoluble in chlorinated solvents of low polarity (*e.g.* $CDCl_3$, CD_2Cl_2). It was, however, sufficiently soluble in $(CD_3)_2CO$ to yield a ^{1}H NMR spectrum which comprised seven equal-intensity signals. However, such a spectrum is incompatible with a 1:1 metal:ligand complex and the chemical shifts of the signals strongly suggest the loss of one of the pyrazolyl rings. A structure which would meet this requirement is the dinuclear structure shown. The chemical shifts for the complex and their assignments corresponding to the labelling are δ 8.42 (A/A'), 7.03 (B/B'), 9.40 (C/C'), 8.05 (D/D'), 6.75 (E/E'), 8.85 (F/F') and 8.25 (G/G'). The evidence for this structure is admittedly tentative but it can only be supposed that the polar solvent is responsible for the cleavage of the 2-pyrazolyl ring of the 1:1 complex followed by dimerization of the bis(pyrazolyl)pyrimidine fragment to give a dinuclear structure. Such a structure, being symmetrical about the C–C bond joining the two pyrimidine rings, can fully account for its solution NMR spectrum.

Dinuclear structures of the type proposed will be quite unstrained since the pair of unco-ordinated pyrazolyl rings will be able to rotate out of the planes of the pyrimidine rings, thus minimizing any steric interactions between the metal moieties and the five-membered rings. Evidence for such non-planar structures has recently been obtained from crystallographic and NMR solution studies of the complexes *fac*-[ReX(CO)$_3$(pbipy)] (X = Cl, Br or I) where pbipy = 6-(pyrazol-1-yl)-2,2′-bipyridine.[15] For example, for the X = Br complex the angle of orientation of the pendant pyrazolyl ring was 36.3 and 48.1° from the plane of the co-ordinated pyridyl ring in two crystallographically independent molecules.

[{ReBr(CO)$_3$}$_2$(tdmpzp)]

The room-temperature ^{1}H NMR spectrum of this complex in CD_2Cl_2 consists of seven signals, comprising three CH signals (intensity ratio 1:1:2) and four methyl signals (intensity ratio 3:3:6:6). Such a pattern is compatible with the 2:1 metal:ligand structure shown at the head of Table 7 (centre). Such a species will possess a symmetry plane passing through the 5-hydrogen (H_G) and the 2-carbon of the pyrimidine ring, assuming that the 2-pyrazolyl ring is undergoing rapid rotation on the ^{1}H NMR timescale. This structure is analogous to the

Table 7 Proton NMR chemical shift data* for $[\{ReBr(CO)_3\}_2(tdmpzp)]$ in CD_2Cl_2 at 303 K



δ							
H_A	H_B	H_C	$H_D/H_{D'}$	$H_E/H_{F'}$	$H_F/H_{F'}$	H_G	Additional signals
2.76	6.18	2.61	2.62	6.36	2.51	6.94	2.77, 7.01, 7.36
(3)	(1)	(3)	(6)	(2)	(6)	(1)	(weak)

* Relative to internal $SiMe_4$ (δ 0). Relative intensities in parentheses.

crystal structure of a bis(dicarbonyldichloro)ruthenium complex of 2,4,6-tris(2-pyridyl)-1,3,5-triazine, containing an additional methoxide group.[16] Such a structure possesses no strong steric interaction between the rhenium(I) moieties and the pendant pyrazolyl ring, in contrast to the alternative structures of this complex (structures **a** and **c**, Table 7) which could be reached by 1,4-metallotropic shifts of either $ReX(CO)_3$ moiety. Evidence for the alternative structures was sought in the solution NMR spectrum of this complex but was not found, despite three weak additional signals being detected. These signals did not show any tendency to exchange with the major set of signals on elevation of solution temperature, as would be required if 1,4-metallotropic shifts were operating. They are therefore attributed to some additional unknown complex species.

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