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A detailed NMR study of the solution stereodynamics in tricarbonylrhenium(I) halide complexes of the non-racemic chiral ligand 2,6-bis[(4R,5R)-4,5-dimethyl-1,3-dioxolan-2-yl]pyridine (L^1) and the molecular structure of fac-[$ReBr(CO)_3(L^1)$]

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Abstract

Tricarbonylrhenium(I) halide complexes of the non-racemic chiral ligand 2,6-bis[(4R, 5R)-dimethyl-1,3-dioxan-2-yl]pyridine (L^1), namely *fac*-[$ReX(CO)_3(L^1)$] (X = Cl, Br or I), have been prepared. In these complexes the ligand is bound in a bidentate fashion, with the N atom of the pyridine ring and an O atom of one of the acetal rings co-ordinated to the octahedral metal centre. The bidentate mode is confirmed by the X-ray structure of *fac*-[$ReBr(CO)_3(L^1)$]. There are four possible diastereoisomers, depending on the configuration at the metal centre and at the acetal-carbon atom of the co-ordinated ring; the X-ray structure of *fac*-[$ReBr(CO)_3(L^1)$] shows that the SR diastereoisomer is present in the solid state. In solution, three of the four possible

diastereoisomers are observed, namely SR, RR and RS; their relative populations are in the order SR > RR > SS. Above ambient temperature the complexes are stereochemically non-rigid. The fluxional kinetics have been measured by a combination of standard band shape analysis and selective inversion experiments. Two distinct processes are present: an acetal *ring flip* and exchange of the pendant and co-ordinated acetal rings. The latter process occurs via two independent mechanisms, namely *tick-tock* and *rotation* pathways. The activation energies for the stereodynamics are in the ranges 72 – 73 kJ mol^{-1} (*tick-tock*), 77 – 78 kJ mol^{-1} (*acetal ring flip*) and 83 – 90 kJ mol^{-1} (*rotation*) at 298 K.

Introduction

Transition metal complexes of ligands that possess redundant donor atoms are potentially fluxional.[1] Recent work by our group has focused on the study of dynamic stereochemical rearrangements in complexes of non-racemic chiral nitrogen donor ligands, such as 2,6-bis[(4S)-alkyloxazolin-2-yl]pyridine (alkyl = methyl or isopropyl).[2,3] The chiral centres on the ligand provide an excellent spectroscopic handle on the mechanism(s) of the fluxions and enable pathways that are otherwise 'invisible' to be elucidated. This paper details the results of studies on the solution stereodynamics of the tricarbonylrhenium(I) halide complexes of the closely related O/N/O hybrid ligand 2,6-bis[(4R, 5R)-dimethyl-1,3-dioxan-2-yl]pyridine (L^1), namely *fac*-[$ReX(CO)_3(L^1)$] (X = Cl, Br or I).

When co-ordinated to a metal centre in a bidentate fashion, potentially (*mer*) terdentate ligands, such as 2,2':6',2''-terpyridine (terpy)[4-6] are fluxional; pendant and

bound donor groups are exchanged. We demonstrated recently that there are two independent mechanisms via which this occurs in systems of like donor atoms (N/N/N), namely a *tick-tock* pathway and a *rotational* pathway.[2] As would be expected, the energetics of these mechanisms are dependent on the nature of the ligand substiuents.[2,3] The question now arises as to the influence of different donor atoms on the stereodynamics. We therefore chose to investigate the tricarbonylrhenium(I) halide complexes of the chiral non-racemic ligand 2,6-bis[(4R, 5R)-dimethyl-1,3-dioxan-2-yl]pyridine (L^1), which undergo similar structural dynamics. Furthermore, these complexes also exhibit reversible 'flip' of the co-ordinated acetal ring,[7] leading to highly complex solution stereodynamics. The asymmetric centres enable the various stereodynamic processes to be elucidated, demonstrating clearly the power of using non-racemic chiral ligands for the measurement of fluxional kinetics.

Experimental

Syntheses

All procedures were carried out under an atmosphere of dry, oxygen-free nitrogen using standard Schlenk techniques. Solvents were dried[8] and degassed before use. The starting materials, purchased from Aldrich Chemical Company, were used without further purification. The pentacarbonylrhenium(I) halides were prepared by standard methods.[9] The ligand, 2,6-bis[(4R, 5R)-dimethyl-1,3-dioxan-2-yl]pyridine (L^1)[10] and the complexes *fac*-[$ReX(CO)_3(L^1)$] (X = Cl, Br or I) were prepared as described below. Analytical data are reported in Table 1.

2,6-Bis[(4R, 5R)-dimethyl-1,3-dioxan-2-yl]pyridine (L^1). 2,6-Pyridinedicarboxaldehyde (1.0 g, 7.4 mmol), (2R, 3R)-butanediol (1.7 cm^3, 18.6 mmol), 2,2-dimethoxypropane (1.0 cm^3, 10.7 mmol), and paratoluenesulfonic acid (*ca*. 40 mg) were refluxed for 72 hours in 30 cm^3 of toluene. The resulting solution was extracted with an aqueous sodium carbonate solution (3 × 30 cm^3) then water (3 × 30 cm^3), dried over $MgSO_4$, and concentrated to dryness *in vacuo*. The solid residue was purified by crystallisation from hot hexane. Yield: 1.5 g, 72%.

Complexes [ReX(CO)$_3$(L^1)] (X = Cl, Br or I). In a typical experiment, *ca*. 0.25 mmol of the appropriate pentacarbonylrhenium(I) halide was refluxed for *ca*. 18 hours with a small excess of the ligand (L^1) in 20 cm^3 of benzene. The benzene was then concentrated to dryness *in vacuo*. The solid residue was crystallised from CH_2Cl_2-hexane solution at –20 ^oC to yield pure, crystalline [ReX(CO)$_3$(L^1)].

Physical methods

Solution ^1H NMR spectra were recorded at McMaster University on a Bruker AM300 Fourier transform spectrometer, operating at 300.13 MHz, in $(CDCl_2)_2$. Chemical shifts are reported in ppm relative to tetramethylsilane as an internal standard. Probe temperatures were controlled by a standard B-VT 2000 unit and are considered accurate to within ± 1 ^oC. Variable temperature experiments were carried out in the temperature range 298 – 393 K; probe temperatures were allowed to equilibrate for *ca*. 15 minuets prior to the acquisition of each spectrum. Band shapes were analysed using the non-iterative simulation program MEX.[11] Inversion-recovery experiments were carried out using our program INVREC2P (modified from the Bruker automation program INVREC), which generates the pulse sequence D1-90^o-τ-90^o-

variable delay-90°-free induction decay. For the non-selective experiments (measurement of T_1) τ was 10 μs. For the selective experiments the signal to be inverted was placed on resonance and τ was $1/2\Delta\nu$ ($\Delta\nu$ is the separation of the inverted and observed signals in Hz). The relaxation delay, D1, was 30 s. 12 – 16 and 24 – 30 experiments (*i.e.* the number of delays in the VD list) were carried out for the non-selective and selective inversions, respectively. Exchange rates were extracted from the longitudinal magnetisations using the program CIFIT.[12] The rate constants obtained from the dynamic NMR spectra were used to calculate the Eyring activation parameters; the errors quoted are those defined by Binsch and Kessler.[13] Two-dimensional exchange (EXSY) spectra were acquired using the Bruker automation program NOESYPH, which generates the program D1-90°-D0-90°-D9-90°-free induction decay. The relaxation delay, D1, was 10 s, the initial value for the evolution delay, D0, was 10 μs, and the mixing time, D8, was 0.5 s. The solid-sate CP MAS ^{13}C NMR spectrum of $[ReBr(CO)_3(L^1)]$ was obtained by Dr A. E. Aliev on a Bruker MSL300, operating at 75.5 MHz. The solution ^{13}C NMR spectra of $[ReBr(CO)_3(L^1)]$ were recorded in $CDCl_3$ on a Jeol GSX 270 operating at 67.94 MHz.

Infrared spectra were obtained as CH_2Cl_2 solutions on a Nicolet 205 FT-IR spectrometer, operating in the region 4000 – 400 cm^{-1}. Mass spectra (LSIMS) were recorded at the London School of Pharmacy on a VG Analytical ZAB-SE4F instrument, using Xe^+ ion bombardment at 8 kV energy. Elemental analyses were performed at University College London.

Crystallography

A single crystal of [$ReBr(CO)_3(L^1)$] of approximate dimensions 0.78 × 0.72 × 0.44 mm was obtained as described above and mounted on a glass fibre. Geometric and intensity data were obtained from this sample using an automatic four-circle Nicolet R3mV diffractometer, using the ω - 2θ technique at 293(2) K. Three standard reflections remeasured every 97 scans, showed no significant loss of intensity during data collection.

Crystal data and data collection parameters. $C_{18}H_{21}BrNO_7Re$, M = 629.47, monoclinic, space group $P2_1$, Mo-K_α radiation (λ = 0.71073 Å), a = 9.231(2), b = 11.296(2), c = 10.975(2) Å, U = 1099.7(4) $Å^3$, Z = 2, D_c = 1.901 mg m^{-3}, μ = 7.378 mm^{-1}, F(000) = 604, data collection range $2.56 \leq \theta \leq 25.29^o$, 4083 reflections collected, 3832 unique (R_{int} = 0.0516).

Structure solution and refinement. Data were corrected for Lorentz-polarisation and absorption effects (ψ scan method; maximum transmission 0.93, minimum transmission 0.19). The structure was solved by direct methods (SHELXS 86)[14] and developed using alternate cycles of least-squares refinement on F^2 and Fourier difference synthesis (SHELXL 93).[15] Non-hydrogen atoms were refined anisotropically, with hydrogen atoms placed in idealised positions [r(CH) = 0.96 Å] and assigned a common isotropic thermal parameter. The final cycle of least-squares included 253 parameters for the 3826 variables. The final *R* and *wR2* values were 0.0435 and 0.1082, respectively [$I > 2\sigma(I)$, 3501 data], and 0.0508 and 0.1225 for all data. The absolute configuration was determined unambiguously using SHELXL 93 procedures; calculated Flack parameter –0.07(2).

Results and discussion

The tricarbonylrhenium(I) halide complexes of the non-racemic chiral ligand, 2,6-bis[(4R, 5R)-dimethyl-1,3-dioxan-2-yl]pyridine (L^1), namely *fac*-[$ReX(CO)_3(L^1)$] (X = Cl, Br or I),were prepared as described and isolated as air-stable crystalline solids. The infrared spectra of the complexes display three carbonyl stretching bands in the region 1850 – 2050 cm^{-1}, characteristic of a facial tricarbonyl metal moiety.[16] Elemental analyses (C, H, and N) are consistent with the formulated species. The mass spectra (LSIMS) do not show any peaks due to the molecular species, $[M]^+$. In each case the highest mass peak corresponds to loss of the pendant acetal ring and the most intense peaks were observed at $m/z^+ = 449$, due to loss of the halogen (X = Cl, Br or I) from this species. In all cases the observed and calculated isotope patterns are fully consistent. Analytical data are reported in Table 1. Analytical and spectroscopic data indicate clearly that the ligand co-ordinates to the metal in a bidentate fashion via the nitrogen donor of the pyridine ring and an oxygen donor of one of the acetal rings. The bidentate bonding is confirmed by the X-ray structure of *fac*-[$ReBr(CO)_3(L^1)$] (see below).

X-Ray structure of *fac*-[$ReBr(CO)_3(L^1)$]

Figure 1 shows the molecular structure of [$ReBr(CO)_3(L^1)$] {L^1 = 2,6-bis[(4R, 5R)-dimethyl-1,3-dioxan-2-yl]pyridine}. Selected bond lengths and angles are reported in Table 2. The structure was obtained to confirm the bidentate bonding mode of the ligand and to determine unambiguously the absolute configuration. Figure 1 shows clearly that the ligand is acting in a bidentate fashion via the pyridine N donor and an acetal O donor, and the absolute configuration (R) at C(2), C(3), C(13), and C(14) is confirmed. The configuration at the metal,[7,17] determined by viewing the molecule

down the pseudo C_3 axis of symmetry (CO ligands down) and assigning priorities to the three remaining donor atoms (Br, O, and N) according to the Cahn-Ingold-Prelog system,[18] is S and the configuration at acetal-carbon atom of the co-ordinated ring C(5) is R.

The geometry at the metal centre deviates somewhat from that of an idealised octahedron. The ligand bite-angle is 74.6(3)°, which compares to 74.7, 74.3, and 72.3°, respectively, for the closely related complexes *fac*-[ReCl(CO)$_3$(L^2)],[2] *fac*-[ReBr(CO)$_3$(terpy)][19] and *cis*-[Mo(CO)$_4$(L^3)][3] {L^2 = 2,6-bis[(4S)-methyloxazolin-2-yl]pyridine, L^3 = 2,6-bis[(4S)-isopropyloxazolin-2-yl]pyridine, terpy = 2,2':6',2''-terpyridine}. There is a corresponding increase in the C(40)-Re-O(1) and C(20)-Re-N(1) angles to 97.3(8) and 104.3(5)°, respectively. There are no significant steric interactions between the metal moiety and the ligand; the shortest non-bonding distance is 3.03 Å [O(3)·····C(20)].

The co-ordinated oxygen atom [O(1)] is close to planar (sum of angles 351.7°) indicating that it tends *towards* sp^2 hybridisation; the dihedral angle between the planes containing C(2)-O(1)-C(5) and Re-O(1)-C(5) is 29.3°. The co-ordinated and pendant acetal rings differ little and both are highly puckered; maximum deviations from the mean planes are 0.228 Å [O(2)] and 0.222 Å [O(3)] for the co-ordinated and pendant rings, respectively.

NMR studies

Ambient temperature (298 K) ^{1}H NMR spectra of the complexes, [ReX(CO)$_3$(L^1)] {X = Cl, Br or I; L^1 = 2,6-bis[(4R, 5R)-dimethyl-1,3-dioxan-2-yl]pyridine}, in $(CDCl_2)_2$

displayed well resolved signals due to the presence of three of the four possible diastereoisomers depicted in Figure 2.[7] The spectra of all three complexes were similar and the results for [ReBr(CO)$_3$(L^1)] will serve to illustrate the analysis of the problem.

The ^{1}H NMR spectrum of [ReBr(CO)$_3$(L^1)] at 298 K comprised two regions of principal interest: (i) the acetal-CH region (*ca.* δ = 6.0 – 6.9) and (ii) the methyl region (*ca.* δ = 1.2 – 1.7). The acetal-CH region displayed three pairs of singlets of widely differing intensity, indicating the presence of three solution-state species (see below). The methyl region displayed twelve overlapping doublets ($^3J_{HH} \approx 6$ Hz); each of the three observed species gives rise to four doublets of equal intensity. The populations of the three species (Table 3) were determined by integration of the acetal-CH signals. The spectrum also displayed signals in the regions δ = 3.5 – 4.6 and 7.4 – 8.4 due to the acetal ring- and pyridine-ring hydrogen nuclides, respectively. The signals in these regions overlapped extensively frustrating complete assignment and accurate measurement of the NMR parameters. Hydrogen-1 NMR data for the complexes [ReX(CO)$_3$(L^1)] {X = Cl, Br or I; L^1 = 2,6-bis[(4R, 5R)-dimethyl-1,3-dioxan-2-yl]pyridine} are reported in Table 3 and the spectrum of [ReBr(CO)$_3$(L^1)] is shown in Figure 3.

If inversion of configuration at the co-ordinated oxygen atom is assumed to be rapid on the NMR chemical shift time-scale, the solution-state species can be assigned to three of the four possible diastereoisomers depicted in Figure 2. The assumption of rapid O inversion is supported by theoretical calculations that predict very low barriers[20,21] and by the X-ray structure of [ReBr(CO)$_3$(L^1)] (see above). This shows

that the co-ordinated oxygen atom is nearly planar, indicating clearly that the ground-state geometry at O is close to the transition-state for pyramidal inversion,[22] suggesting a low barrier to inversion.

The assignment of the major solution-state species to the SR diastereoisomer (letters refer to the configuration at the metal and acetal-carbon atom of the co-ordinated acetal ring, respectively) was based on the X-ray structure of [$ReBr(CO)_3(L^1)$] (see above). In the solid-state [$ReBr(CO)_3(L^1)$] exists exclusively as the SR diastereoisomer and this is presumed to predominate in solution. Attempts to confirm this by comparison of the solid-state and solution ^{13}C NMR spectra of [$ReBr(CO)_3(L^1)$] were not conclusive; the chemical shifts of the major species (in solution) correlate well with those of the solid-state species, but are not sufficiently sensitive to exclude the other possibilities, given the small changes in shift that occur on dissolution. The high frequency signal of the SR diastereoisomer was assigned to the acetal-CH of the co-ordinated ring on the basis of its chemical shift.[7] The assignment of the other solution-state species to the RR and SS diastereoisomers was based on the dynamic NMR spectra (see below).

Three distinct dynamic processes are expected[2,3,7] [all of which are observed (see below)], namely (i) exchange of pendant and co-ordinated acetal rings via a *rotation* mechanism, (ii) exchange of pendant and co-ordinated acetal rings via a *tick-tock* mechanism, and (iii) *flip* of the co-ordinated acetal ring. The exchange of pendant and co-ordinated rings via the *rotation* mechanism (Figure 4a) is easy to distinguish since it does not lead to any diastereoisomerisations. This is the highest energy process (see below). The *tick-tock* process (Figure 4b) leads to inversion of

configuration at the metal and *may* also lead to inversion of configuration at the acetal-carbon atom of the co-ordinated ring. The acetal *ring flip* process (Figure 4c) leads to formal inversion of configuration at the acetal-carbon atom, but not at the metal. The *tick-tock* and *ring flip* processes are difficult to distinguish, but previous studies on analogous systems[2,3,7,23] suggest that the *tick-tock* fluxion is likely to be more facile than the *ring flip*. Magnetisation transfer experiments (EXSY and selective inversions) show clearly that exchange occurs initially between the SR diastereoisomer and the second most abundant species. If it is assumed that these magnetisation transfers result from the *tick-tock* fluxion (see above) then the configuration at the metal in this diastereoisomer can be assigned as R. The configuration at the acetal-carbon atom can not be inferred, but it is thought most likely to have the R configuration; steric interaction between the acetal-methyls and the metal moiety are less than if the carbon atom adopts the S configuration. At slightly higher temperatures, the SR diastereoisomer begins to exchange with the minor species, which was assigned as SS, on the assumption that this arises from the acetal *ring flip* fluxion (see above). Assignments are clearly not unambiguous, but the relative populations of the diastereoisomers [SR > RR > SS, (Table 2)], follow the trend expected on steric grounds. The chemical shifts of the signals due to the acetal-carbon hydrogens of the co-ordinated ring are consistent with those for the closely related complexes, $[ReX(CO)_3(L^4)]$ {X = Cl, Br, I; L^4 = 2-[(4R, 5R)-dimethyl-1,3-dioxan-2-yl]pyridine},[7] lending support to these assignments.

Dynamic NMR studies were performed on the three complexes, $[ReX(CO)_3(L^1)]$, in the temperature range 298 – 398 K. On warming, fully reversible band shape changes were observed in all regions of the spectra, but the acetal-CH signals are most

amenable to analysis, so were used for the measurement of the exchange kinetics. A two-dimensional exchange (EXSY) spectrum at 298 K (mixing time, D8 = 0.5 s) displayed cross peaks between the bands of the SR and RR diastereoisomers as a result of exchange between acetal rings via the *tick-tock* pathway (Figure 4b).[2,3] The exchange kinetics were measured in the slow exchange regime using the selective inversion-recovery technique.[24-27] The signal due to the acetal-CH of the co-ordinated acetal ring of the SR diastereoisomer was selectively inverted at 298 and 303 K; magnetisation transfer to the acetal-CH signal of the pendant ring of the RR diastereoisomer was clearly observed, enabling accurate rates to be measured. Experiments were repeated, inverting the acetal-CH signal of the pendant ring of the SR diastereoisomer; rates are identical within experimental error (± 5 – 10%).

On warming further, the acetal-CH signals of the SS diastereoisomer also began to exhibit reversible broadening due to SR ⇆ SS magnetisation transfers, resulting from the *flip* of the co-ordinated acetal ring[7] (Figure 4c). Rates in the intermediate exchange regime were measured by total band shape analysis.[28] In solution, each diastereoisomer exists as a pair of degenerate species, depending on which of the two acetal rings is metal co-ordinated [see Figure 4(a)], giving a total of twelve solution-state species, all of which must be considered. Since there are no scalar couplings between the pendant and co-ordinated acetal rings, this simplifies to the six-spin system problem, (I) [letters in parentheses indicate the signals due to the pendant (p) and co-ordinated (c) acetal rings].

Spin system:	1	2	3	4	5	6
Assignments:	SR(c)	SR(p)	RR(c)	RR(p)	SS(c)	SS(p)
Rates:	k_{12}	k_{13}	k_{14}	k_{15}	k_{16}	
	k_{23}	k_{24}	k_{25}	k_{26}		
	k_{34}	k_{35}	k_{36}			
	k_{45}	k_{46}				
	k_{56}					

(I)

The variable temperature ^{1}H NMR spectra were simulated on this basis. At moderate temperatures (< 363 K) spectra were simulated accurately using four non-zero rate constants (all other rates being negligible), namely k_{14} and k_{23} (*tick-tock*), and k_{15} and k_{26} (*acetal ring flip*). Above *ca*. 363 K it was also necessary to use non-zero rate constants for k_{12}, k_{34}, and k_{56} (*rotation*). Although the rates of *rotation* would be expected to be different for the three diastereoisomers, spectra were simulated using equal rates for the three processes, because of the problems of fitting the experimental spectra to a large number of independent variables. It seems unlikely that the energetics of the *rotation* differ greatly between diastereoisomers and the assumption is considered valid. Sixteen spectra were simulated, six of which are shown in Figure 5.

The rate data measured by the band shape analyses and selective inversion experiments were used to determine the activation parameters from a least-squares fitting of the linearised Eyring equation. Activation parameters for the complexes,

$[ReX(CO)_3(L^1)]$ {X = Cl, Br, I; L^1 = 2,6-bis[(4R, 5R)-dimethyl-1,3-dioxan-2-yl]pyridine} are reported in Table 4.

Fluxional Behaviour

Analysis of the variable temperature ^1H NMR spectra of the complexes $[ReX(CO)_3(L^1)]$ (see above) shows clearly that three independent fluxional processes (depicted in Figure 4) are occurring; these are discussed below.

The *rotation* mechanism[2,3] (Figure 4a) leads to exchange of the pendant and co-ordinated acetal rings, without diastereoisomerisation. The free energies of activation (Table 4) are similar to those observed previously for analogous process in the tricarbonylrhenium(I) halide complexes of the bis(oxazoline) 2,6-bis[(4S)-methyloxazolin-2-yl]pyridine (L^2), namely $[ReX(CO)_3(L^2)]$ (X = Cl, Br or I).[2] The principal contribution to $\Delta G^{\ddagger}$ is presumably the energy required to break the R-O(acetal) bond, which is necessarily cleaved. The similar magnitudes for the free energies of activation thus indicate that the Re-O(acetal) and Re-N(oxazoline) bond strengths are similar in these complexes. The halide dependence on the energetics of the *rotation* appears significant and may be due in part to the increasing size of the halide, but is more likely a consequence of the narrow temperature range over which the kinetics were measured. The moderately large errors associated with the activation parameters are also due to the narrow temperature range.

The *tick-tock* and acetal *ring flip* fluxions lead to exchange between diastereoisomers and are difficult to distinguish unambiguously. Both processes have been observed previously in tricarbonylrhenium(I) complexes of acetal ligands. The energetics of

the *tick-tock* fluxion are considerably lower [$\Delta G^{\ddagger}$(298 K) ≈ 59 – 62 kJ mol^{-1}][23] than those of the *ring flip* [$\Delta G^{\ddagger}$(298 K) ≈ 84 – 88 kJ mol^{-1}].[7] It was therefore assumed that the *tick-tock* fluxion was more facile than the acetal *ring flip* in the complexes [ReX(CO)$_3$(L^1)]; the process with the lowest activation barrier (Table 4) was thus attributed to the *tick-tock* exchange of the pendant and co-ordinated acetal rings.

The free energies of activation for the *tick-tock* fluxion are in the narrow range 72 – 73 kJ mol^{-1} and show only minimal halide dependence. The magnitudes of $\Delta G^{\ddagger}$ (298 K) are similar to those measured for the tricarbonylrhenium(I) halide complexes of L^2,[2] but are lower than those of L^3.[3] The factors that affect fluxional energetics are complex and the origin of the barrier in the *tick-tock* fluxion is not entirely clear; electronic and geometric factors must both contribute. The *tick-tock* fluxion is presumably initiated by the interaction of one of the donor atoms on the pendant ring with the metal centre. The energetics will presumably reflect the ease of interaction of the pendant ring with the metal and the strength metal-donor atom bond of the co-ordinated ring. The molecular structures of [ReX(CO)$_3$(L^1)] (see above) and [ReX(CO)$_3$(L^2)][2] show that the ligands are geometrically similar (*e.g.* ligand bite angles are identical within experimental error) and there are no significant steric interaction between the ligands and the metal centre in either case. It therefore seems reasonable to conclude that the Re-O(acetal) and Re-N(oxazoline) bonds strengths are approximately equal in these complexes. This is supported by the fact that the energetics of the *rotation* mechanism are also similar in these complexes (see above).

The *flip* of the acetal ring leads to inversion of configuration at the acetal-carbon atom of the co-ordinated acetal ring. The two possible mechanisms proposed for the acetal

ring flip[7] are depicted in Figure 6. Mechanism (i) involves cleavage of the Re-O bond, yielding a five co-ordinate transition state, followed by formation of a new Re-O bond. Mechanism (ii) involves loosening of the Re-O bond, concomitant with the formation of a pseudo seven co-ordinate transition state. Previously it had been concluded (tentatively) that mechanism (i) was the most likely because of the relatively high barriers observed for the *ring flip* in the complexes $[ReX(CO)_3(L^4)]$ {X = Cl, Br or I; L^4 = 2-[(4R, 5R)-dimethyl-1,3-dioxan-2-yl]pyridine.[7] If this were the mechanism, one might expect the acetal *ring flip* and *rotation* mechanisms to have similar barrier heights (since both would involve Re-O bond cleavage), which is clearly not the case; barrier heights for the *rotation* are *ca*. 6 – 11 kJ mol^{-1} greater than for the *ring flip* (Table 4). This suggests that mechanism (ii), which involves loosening, rather than cleavage, of the Re-O bond is operative. This is consistent with the low entropies of activation observed for both series of complexes (Table 4 and reference 7). It is also noteworthy that the absolute magnitudes for the *ring flip* in the complexes of L^1 are 8 – 11 kJ mol^{-1} less than in the complexes of L^4.[7] It may be that the presence of the pendant acetal ring modifies the mechanism of the *ring flip* (see above), although this is considered unlikely. The lowering of the free energy of activation for the acetal *ring flip* in the complexes of L^1 is presumably a direct consequence of the *tick-tock* fluxion loosening the Re-O interaction.

Conclusion

The ligand, 2,6-bis[(4R, 5R)-dimethyl-1,3-dioxan-2-yl]pyridine (L^1) complexes to the halogenotricarbonylrhenium(I) metal moieties in a bidentate fashion via the pyridine N atom and an O atom of one of the acetal rings. The resultant compounds, $[ReX(CO)_3(L^1)]$ (X = Cl, Br or I), undergo three independent fluxional processes,

namely exchange of the pendant and co-ordinated acetal rings by *tick-tock* and *rotation* mechanisms, and a *flip* of the co-ordinated acetal ring. Rates of the stereodynamics were measured in the slow and intermediate exchange regimes by selective inversion experiments and standard band shape analysis, respectively. The free energies of activation for the *tick-tock* and *rotation* fluxions are close to those measured previously for the related bis(oxazoline) complexes, $[ReX(CO)_3(L^2)]$ {X = Cl, Br or I; L^2 = 2,6-bis[(4S)-methyloxazolin-2-yl]pyridine}. The mechanism of the acetal ring flip remains a matter of conjecture, but results reported here point towards a mechanism that involves both oxygen atoms of the acetal ring loosely bound to the metal in the transition state, contrary to our previous results.[7]

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