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Stereochemical rearrangements in tricarbonylrhenium(I) halide complexes of the non-racemic chiral ligand 2-[(4R),(5R)-dimethyl-1,3-dioxan-2-yl]pyridine (L): a dynamic NMR study.

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Abstract

Tricarbonylrhenium(I) halide complexes of the non-racemic chiral ligand 2-[(4R),(5R)-dimethyl-1,3-dioxan-2-yl]pyridine (L), namely *fac*-[ReX(CO)$_3$L] (X = Cl, Br or I), have been prepared and their latent fluxionality studied by dynamic NMR techniques in the slow and intermediate exchange regimes. In solution, these complexes give rise to four diastereoisomers, depending on the configuration at the metal and at the acetal-carbon atom, respectively; the relative populations are in the order SR > RR >> RS > SS. At moderate temperatures, a reversible 'acetal ring flip' leads to *formal* inversion of configuration at the acetal-carbon atom; the free energies of activation are in the range 84 - 88 kJ mol^{-1} at 298 K. Above *ca*. 370 K, reversible

ligand dissociation also occurs, leading to an exchange of all four diastereoisomers on the NMR chemical shift time-scale.

Introduction

Non-racemic chiral ligands play an important role in organometallic chemistry, particularly in homogeneous catalysis;[1] understanding the bonding in these complexes is therefore of importance. The systematic study of fluxional processes provides a sensitive method for probing bonding interactions, particularly where multiple mechanistic pathways are competing. We have demonstrated recently that non-racemic chiral ligands can be used to elucidate dynamic processes that are otherwise unobservable,[2,3] providing detailed information on the bonding between the metal and the fluxional ligand. This paper illustrates the power of such an approach for the study of complex fluxional organometallic systems.

The latent fluxionality of transition metal complexes of potentially *mer*-terdentate ligands, in which the ligand is restricted to a bidentate bonding mode, is of current interest.[4,5] The possible mechanisms of the dynamics are the subject of controversy.[6,7] Our approach has been to employ a non-racemic chiral oxazoline ligand;[8] the spectroscopic handle provided by the asymmetric centres enables the mechanism to be determined unambiguously. Furthermore fluxional pathways that are otherwise 'invisible' can be elucidated. We reported recently on the use of the C_2-symmetric bis(oxazolines), 2,6-bis[(4S)-alkyloxazolin-2-yl]pyridine (alkyl = methyl or isopropyl), as a mechanistic probe for the dynamic stereochemical rearrangements in complexes of the type shown in Figure 1.[2,3] This paper describes the results of a detailed dynamic NMR study on the tricarbonylrhenium(I) halide complexes of the

closely related acetal ligand, 2-[(4R),(5R)-dimethyl-1,3-dioxan-2-yl]pyridine (L), namely *fac*-[ReX(CO)$_3$L] (X = Cl, Br or I).

Experimental

Syntheses

All manipulations were performed using standard Schlenk techniques[9] under an atmosphere of dry, oxygen-free nitrogen. Solvents were dried[10] and degassed before use. The pentacarbonylrhenium(I) halides were prepared according to previously published proceedures.[11] (2R),(3R)-Butanediol, 2-pyridinecarboxaldehyde, and 2,2-dimethoxpropane were purchased from Aldrich Chemical Company, and were used without further purification. The compounds were prepared as described below. Analytical and ^{1}H NMR data are reported in Tables 1 and 2, respectively.

2-[(4R),(5R)-dimethyl-1,3-dioxan-2-yl]pyridine (L).[12] 2-Pyridinecarboxaldehyde (1.0 cm^3, 10.5 mmol), (2R),(3R)-butanediol (1.5 cm^3, 16.43 mmol), 2,2-dimethyoxypropane (1.5 cm^3, 16 mmol), and *ca*. 40 mg of paratoluenesulfonoic acid were refluxed for 48 hours in 30 cm^3 of toluene. The toluene was then extracted with (i) aqueous Na_2CO_3 solution and (ii) water. After drying ($MgSO_4$), the toluene was concentrated *in vacuo* to yield an oil. The ligand, 2-[(4R),(5R)-dimethyl-1,3-dioxan-2-yl]pyridine, was crystallisation from hot hexane. Yield: 1.40 g, 75%.

The three complexes, [ReX(CO)$_3$L] (X = Cl, Br or I), were prepared similarly, as illustrated by procedure for the complex X = Br.

{2-[(4R),(5R)-dimethyl-1,3-dioxan-2-yl]pyridine}bromotricarbonylrhenium(I). 100 mg (0.246 mmol) of [$ReBr(CO)_5$] and 50 mg (0.279 mmol) of 2-[(4R),(5R)-dimethyl-1,3-dioxan-2-yl]pyridine were refluxed for *ca*. 18 hours in 20 cm^3 of benzene. The solvent was then removed *in vacuo* to yield an oil that was purified by precipitation from a CH_2Cl_2-hexane solvent mixture at -20 ^oC. Yield: 72 mg, 60%.

Physical methods

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

Hydrogen-1 NMR spectra were recorded in $[D]_2$-tetrachloroethane at McMaster University on a Bruker AM300 Fourier transform spectrometer, operating at 300.13 MHz. Chemical shifts are quoted 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. Standard one-dimensional variable temperature experiments were carried out in the temperature range 303 - 393 K; probe temperatures was allowed to equilibrate for *ca*. 20 minuets before each spectrum was recorded. Acquisition times were typically *ca*. 5 s, and a relaxation delay of 5 s was allowed between scans. Band shapes were analysed using the non-iterative simulation program MEX.[13] Inversion-recovery experiments were carried out using the Bruker automation program INVREC2P, which generates the pulse sequence D1-90-τ-90-VD-90-free induction decay. For non-selective inversions the delay, τ, was 10 μs.

For the selective experiments, the signal to be inverted was placed on resonance and τ was set at $1/(2\Delta\nu)$; $\Delta\nu$ is the frequency difference between the inverted and observed signals. The relaxation delay, D1, was 30 s. For the selective- and non-selective inversions, respectively, 24 - 30 and 12 - 16 experiments (*i.e.* the number of delay times in the VD list) were carried out. Exchange rates were extracted from the longitudinal magnetisations using the program CIFIT.[14] Two-dimensional exchange (EXSY) spectra, recorded using the Bruker automation program NOESYPH, were acquired prior to the selective inversions, to ascertain which signals were undergoing chemical exchange. Typical acquisition parameters for the EXSY experiment are described elsewhere.[3] The rate constants obtained from the dynamic NMR experiments were used to calculate the Eyring activation parameters; the errors quoted are those defined by Binsch and Kessler.[15]

Results

The three complexes, $[ReX(CO)_3L]$ (X = Cl, Br or I; L = 2-[(4R),(5R)-dimethyl-1,3-dioxan-2-yl]pyridine), were isolated as air-stable brown oils as described above. The mass spectra (LSIMS) of the complexes displayed strong peaks due to the species $[M-H]^+$, due to the loss of the acetal carbon-H, and $[M-X]^+$ (X = Cl, Br or I); the observed and calculated isotope patterns are consistent. The infrared spectra (CH_2Cl_2 solution) displayed three carbonyl stretching bands in the region 1850 - 2050 cm^{-1}, as expected for a fac-octahedral tricarbonylrhenium(I) complex.[16] Analytically pure samples could not be obtained; consequently, elemental analyses (C, H and N) gave poor data. Data are reported in Table 1.

NMR studies

The ambient temperature (303 K) ^{1}H NMR spectra of the complexes, [ReX(CO)$_3$L] (X = Cl, Br or I; L = 2-[(4R),(5R)-dimethyl-1,3-dioxan-2-yl]pyridine), in [D]$_2$-tetrachloroethane displayed well-resolved signals due to the presence of four non-exchanging diastereoisomers (Fig. 2). The spectra of the three complexes were similar and the results obtained for [ReBr(CO)$_3$L] will serve to illustrate the analysis of the problem.

The ^{1}H NMR spectrum of [ReBr(CO)$_3$L] at 303 K displayed signals in two regions of principle interest (Fig. 3): (i) acetal-methyl region (*ca.* ∂ = 1.1 - 1.7) and (ii) acetal-CH region (*ca.* ∂ = 6.0 - 7.0). The acetal-methyl region displayed four pairs of doublets ($^3J_{HH} \approx 6$ Hz) of differing intensity. If it is assumed that inversion of configuration at the co-ordinated oxygen atom is rapid on the NMR chemical shift time-scale,[17,18] the four pairs of doublets can be assigned to the four (non-exchanging) diastereoisomers shown in Figure 2. These are labelled SR, RR, RS, and SS [depending on the configuration at the metal and at the acetal-carbon atom (C_1, see Figure 2), respectively]. The configuration at the metal[19] (R or S) was determined by viewing the molecule down the pseudo C_3 axis of symmetry (with the three CO ligands down) and assigning priorities to the three remaining ligands (halogen, oxygen and nitrogen), according to the Cahn-Ingold-Prelog system.[20]

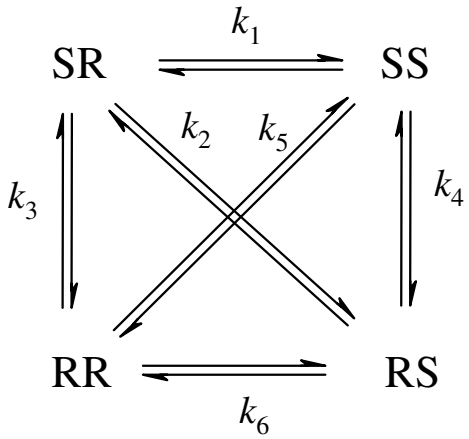
The acetal-CH region displayed four broad singlets, assignable to the four diastereoisomers. The line broadening of these signals results from unresolved long-range couplings to the pyridine-H nuclides. The assignment of the major solution-state diastereoisomer was based on our preliminary results on the closely related

complex, $[ReBr(CO)_3L^2]$ {L^2 = 2,6-bis[(4R),(5R)-dimethyl-1,3-dioxan-2-yl]pyridine}, which has four directly analogous diastereoisomers in solution. In the solid-state $[ReBr(CO)_3L^2]$ exists exclusively as the SR diastereoisomer, and (solid-sate and solution) ^{13}C NMR data indicate that it predominates in solution. The major solution-state species of the complex $[ReBr(CO)_3L]$ {L = 2-[(4R),(5R)-dimethyl-1,3-dioxan-2-yl]pyridine} was therefore assigned as the SR diastereoisomer. The assignments of the remaining signals are based on the variable temperature ^1H NMR spectra (see below) and the relative chemical shifts of the acetal-CH signals. Exchange can occur between diastereoisomers (SR ⇆ SS and RS ⇆ RR) as a result of an 'acetal ring flip' process, which leads to *formal* inversion of configuration at the acetal carbon atom, C_1 (see below). There is no exchange between these pairs because, at moderate temperatures (see below), there is no mechanism for *formal* inversion of configuration at the metal centre. The signals due to the SS diastereoisomer is thus readily identified because it exchanges with the signal due to the SR diastereoisomer (see above). The acetal-CH of the SR diastereoisomer is oriented on the same side as the halogen (Br) and resonates at higher frequency than the acetal-CH of the SS diastereoisomer. The acetal-CH of the RS diastereoisomer is also oriented on the same side as the halogen, so might be expected to resonate at higher frequency than the acetal-CH of the RR diastereoisomer. Thus the high frequency acetal-CH signal of the RR/RS pair was assigned to the RS diastereoisomer. This is not unambiguous, but the *absolute* assignments do not affect the analysis of the dynamic exchange problem. The populations (Table 2), determined from the relative intensities of the acetal-CH signals, are in the order SR > RR >> RS > SS.

The ^{1}H NMR spectrum of [ReBr(CO)$_3$L] also displayed signals in the regions *ca.* δ = 3.6 - 4.6 and 7.2 - 9.0, due to the hydrogen nuclides of the acetal and pyridine rings, respectively. The signals of the four diastereoisomers are not well separated in these regions, frustrating complete assignment and accurate measurement of all chemical shifts and scalar couplings. Hydrogen-1 NMR data for the ligand (L), {2-[(4R),(5R)-dimethyl-1,3-dioxan-2-yl]pyridine}, and the three complexes, [ReX(CO)$_3$L] (X = Cl, Br or I), are given in Table 2.

Variable-temperature dynamic ^{1}H NMR experiments were carried out on all three complexes in the temperature range 303 - 393 K. The signals of the acetal-CH nuclides (H_A, see Figure 2) provide the most suitable spectroscopic handle on the kinetics. Above *ca.* 330 K, the acetal-CH signals due to the minor species (RS and SS) broaden quickly, as a consequence of exchange between pairs of diastereoisomers, *i.e.* SR ⇆ SS and RR ⇆ RS. Rates were measured in the slow exchange regime by selective inversion experiments[21-24] and in the intermediate exchange regime by standard band shape analysis.[25] The acetal-CH signals of the two major diastereoisomers, SR and RR, were selectively inverted at 323 and 328 K. At these temperatures, magnetisation transfers were only observed between pairs of diastereoisomers (SR ⇆ SS and RR ⇆ RS), as a consequence of *formal* inversion of configuration at the acetal-carbon atom. This presumably arises from an 'acetal ring flip' that leads to exchange of the co-ordinated and pendant oxygen atoms. No magnetisation transfers were observed between the SR/SS pair and the RR/RS pair, showing clearly that there is no *formal* inversion of configuration at the metal centre (R ⇆ S) at these temperatures. Spectra for the selective inversion of the RR diastereoisomer at 323 K are shown in Figure 4. Kinetic data are reported in Table 3.

Analysis of the variable temperature ^{1}H NMR line shapes of the acetal-CH signals was carried out according to the dynamic spin system (I)



(I)

The six possible rate constants were treated as independent variables in the analysis. Below *ca*. 370 K, band shapes could only be simulated accurately with two non-zero rate constants, namely k_1 and k_6, corresponding to the *formal* inversion of configuration at C_1 (Fig. 2). At temperatures in excess of 370 K, the band shape analysis indicated the onset of a second dynamic process on the NMR chemical shift time-scale. Accurate simulation of the high temperature spectra required the use of equal, non-zero rate constants for k_2, k_3, k_4 and k_5, in addition to the non-zero rates for k_1 and k_6. This second process is presumed to involve ligand dissociation; the process is fully reversible and there was no evidence of decomposition. Twelve reliable fits were obtained, seven of which are shown in Figure 5. Kinetic data are reported in Table 3 and the Eyring activation parameters are reported in Table 4. Band shape

changes, consistent with the above analysis, were also observed in the other regions of the variable temperature ^{1}H NMR spectra (see above).

The compounds [ReX(CO)$_3$L] {X = Cl or I; L = 2-[(4R),(5R)-dimethyl-1,3-dioxan-2-yl]pyridine} behaved analogously and the dynamic NMR spectra were analysed on the same basis as (see above). However, the signal due to the SS diastereoisomer of the iodide complex was obscured by the residual solvent signal (δ = 5.96) frustrating a full analysis of the RS ⇆ SS kinetics; acceptable fits of the experimental spectra were obtained using equal rates for the two independent acetal ring flip processes.

Discussion

Variable temperature ^{1}H NMR data show clearly that, at moderate temperatures, a (reversible) *formal* inversion of configuration occurs at the acetal-carbon atom, C_1, causing an interconversion between pairs of diastereoisomers (SR ⇆ SS and RR ⇆ RS). This formal inversion of configuration presumably results from an acetal ring flip process that exchanges the co-ordinated and pendant oxygen donor atoms. Two possible mechanisms, shown in Figure 6, can be envisaged for the acetal ring flip. Mechanism (i) (Fig. 6) involves cleavage of the Re-O bond, yielding a five co-ordinate transition state, followed by the formation of a new Re-O bond. Mechanism (ii) involves a loosening of the Re-O bond, concomitant with the formation of a pseudo seven co-ordinate transition state. The small magnitudes for the entropy of activation, $\Delta S^{\ddagger}$, (Table 4) point towards an associated transition state of the type involved in mechanism (ii). Conversely, the free energies of activation [$\Delta G^{\ddagger}$(298 K) ≈ 84 - 88 kJ mol^{-1}] indicate that Re-O bond cleavage is involved; data are comparable to

the activation energies for the cleavage of the Re-N bond in the closely related complexes [$ReX(CO)_3L^3$] {X = Cl, Br or I; L^3 = 2,6-bis[(4S)-methyloxazolin-2-yl]pyridine}.[2] This suggest mechanism (i) (Fig. 6) is preferred. Although entropy of activation data provide information about the structure of the transition state, they are generally a less reliable indicator than energy of activation data. For this reason we consider mechanism (i) (Fig. 6) most likely, but more work is clearly necessary to establish this. We are currently investigating complexes of the analogous ligand 2-[(4R),(6R)-dimethyl-1,3-dioxan-2-yl]pyridine, to gain further insight.

The magnitudes of the free energies of activation for the SR → SS processes are *ca*. 2 - 4 kJ mol^{-1} greater than for the RR → RS process; this is higher than expected from the relative ground state energies of the two diastereoisomers. This indicates that the transition state species of the two processes are subtly different, which is difficult to rationalise, particularly in terms of mechanism (i). The effect of the halogen on the dynamics appears to be minimal; this is expected because the halide is *cis* to the fluxional ligand.

Ring flip processes of this type are novel in tricarbonylrhenium(I) halide complexes, but a similar behaviour has been observed previously in palladium(II) complexes of bipyrimidine (bipym).[26] The tricarbonylrhenium(I) halide complexes of bipym, *fac*-[$ReX(CO)_3$(bipym)] (X = Cl, Br or I), do not shown analogous fluxional behaviour at a measurable rate on the NMR time-scale.[27]

Above *ca*. 370 K, the band shape changes indicate that the ligand is undergoing a reversible dissociation from the metal centre (see above), leading to an averaging of

all four diastereoisomers. Only two or three reliable rate constants were obtained for this process and the energy data obtained must therefore be treated with some caution. The principle contribution to $\Delta G^{\ddagger}$ probably comes from the energy require to break the Re-N(pyridine) bond. The higher magnitudes for the ligand dissociation, compared to the acetal ring flip fluxion (see above), presumably reflect the differences in the Re-O and Re-N bond strengths. The considerably higher magnitude of $\Delta G^{\ddagger}$ obtained for the chloro-complex is not thought significant; experimental errors, consequential of the narrow temperature range, are the most likely explanation.

Conclusion

The complexes [ReX(CO)$_3$L] {X = Cl, Br or I; L = 2-[(4R),(5R)-dimethyl-1,3-dioxan-2-yl]pyridine} give rise to four diastereoisomers in solution. At moderate temperatures an acetal ring flip process leads to exchange of the pendant and co-ordinate oxygen atoms, causing formal inversion of configuration at the acetal carbon atom. The kinetics of the acetal ring flip were measured in the slow and intermediate exchange regimes and the results indicate that the mechanism involves initial cleavage of the Re-O(acetal) bond, concomitant with the formation of a five co-ordinate transition state.

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References

1. J. P. Collman, L. S. Hegedus, J. R. Norton and R. G. Fink, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, California, USA, 1987.
2. P. J. Heard and C. Jones, J. *Chem. Soc., Dalton Trans*., 1997, 1083.
3. P. J. Heard and D. A. Tocher, . *Chem. Soc., Dalton Trans*., 1998, 2169.
4. A. Gelling, M. D. Olsen, K. G. Orrell, A. G. Osborne and V. Šik, *J. Chem. Soc., Dalton Trans*., 1998, 3479, and references therein.
5. A. Gelling, K. G.Orrell, A. G. Osborne, V. Šik, M. B. Hursthouse, D. E. Hibbs and K. M. A. Malik, *J. Chem. Soc., Dalton Trans*., 1998, 2151, and references therein.
6. E. Rotondo, G. Giordano and D. Minniti, *J. Chem. Soc., Dalton Trans*., 1996, 253.
7. E. W. Abel, A. Gelling, K. G. Orrell, A. G. Osborne and V. Šik, *J. Chem. Soc., Chem. Commun*., 1996, 2329.
8. T. G. Grant and A. I. Meyers, Tetrahedron, 1994, **50**, 2297.
9. D. F. Shriver, *Manipulation of Air-sensitive Compounds*, McGraw-Hill, New York, 1969.
10. D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, Pergamon, Oxford, 1988.
11. S. P. Schmidt, W. C. Trogler and F. Basolo, *Inorg. Synth*., 1979, **28**, 160.
12. F. A. J. Meskens, *Syntheses*, 1981, 501.
13. A. D. Bain and G. J. Duns, *Can. J. Chem*., 1996, **74**, 819.
14. A. D. Bain and J. A. Cramer, *J. Mag. Reson*., 1996, **118**, 21.
15. G. Binsch and H. Kessler, *Angew. Chem., Int. Ed. Engl*., 1980, **19**, 411.
16. D. A. Edwards and J. Marshalsea, *J. Organomet. Chem*., 1977, **131**, 73.
17. W. Cherry and N. Epiotis, *J. Am. Chem. Soc*., 1976, **98**, 1135.

18. R. F. W. Bader, J. R. Cheeseman, K. E. Wiberg and C. Breneman, *J. Am. Chem. Soc*., 1990, **112**, 6530.

19. E. W. Abel, K. Kite and P. S. Perkins, *Polyhedron*, 1987, **6**, 319, and references therein.

20. E. L. Eliel and S. H. Wilen, *Stereochemistry of Organic Compounds*, Wiley, New York, 1994.

21. A. D. Bain and J. A. Cramer, *J. Phys. Chem*., 1993, **97**, 2884.

22. A. D. Bain and J. A. Cramer, *J Magn. Reson*., 1993, **103 A**, 217.

23. S. Forsen and R. A Hoffman, *J. Chem. Phys*., 1963, **39**, 2892.

24. R. E. Hoffman and S. Forsen, *Prog. Nucl. Magn. Reson. Spectrosc*., 1966, **1**, 15.

25. J. Sandström, *Dynamic NMR Spectroscopy*, Academic Press, New York, 1982.

26. J. G. P. Delis, P. G. Aubel, K. Vrieze and P. W. N. M. van Leeuwen, *Organometallics*, 1997, **16**, 2948.

27. E. W. Abel, P. J. Heard and K. G. Orrell, unpublished results.

Table 1. Analytical data for the complexes $[ReX(CO)_3L]$

Complex	Yield[a]	Infrared data[b]/cm^{-1}	Mass Spectral data[c]	Analyses[d]		
				C	H	N
$[ReCl(CO)_3L]$	72	2031	484 $[M-H]^+$	29.81 (32.20)	2.25 (2.70)	2.36 (2.89)
		1925	450 $[M-Cl]^+$			
		1899				
$[ReBr(CO)_3L]$	60	2032	528 $[M-H]^+$	27.86 (29.50)	2.17 (2.47)	2.31 (2.64)
		1927	500 $[M-H-CO]^+$			
		1900	449 $[M-H-Br]^+$			
$[ReI(CO)_3L]$	39	2031	576 $[M-H]^+$	26.08 (27.09)	1.99 (2.27)	2.08 (2.43)
		1928	548 $[M-H-CO]^+$			
		1902	449 $[M-H-I]^+$			

[a] Percentage yield relative to $[ReX(CO)_5]$.

[b] Carbonyl stretching modes; recorded as CH_2Cl_2 solutions.

[c] LSIMS Mass spectral data.

[e] Calculated analyses in parentheses.

Table 2. Hydrogen-1 NMR data[a] for the complexes $[ReX(CO)_3L]$.

Complex	Diastereoisomer[b]	δ(acetal-C**H**$_3$)	δ(acetal ring-**H**)	δ(acetal C-**H**)	δ(pyridine-**H**)[c]
Ligand (L)[d]		1.32 (5.6); 1.27 (5.6)	3.79 (5.6; 7.6); 3.76 (5.6; 7.6)	5.91	8.55 (4.8); 7.66 (7.8; 7.5); 7.50 (7.8); 7.19 (4.8; 7.5)
$[ReCl(CO)_3L]$	SR (58)	1.56 (6.1); 1.36 (6.1)	4.01 (6.1; 8.6); 3.79 (6.1; 8.6)	6.61	8.75 (5.5); 7.99 (8) ; 7.63 (8; 8); 7.50 (8; 5.5)
	RR (37)	1.43 (6.1); 1.33 (6.1)	4.40 (6.1; 8.6); 4.03 (6.1; 8.9)	6.15	8.72 (5.5); 8.01 (8); 7.63 (8; 8); 7.47 (8; 5.5)
	RS (4.5)	1.51 (6.3); 1.30 (5.9)	4.24	6.73	
	SS (0.5)			6.08	
$[ReBr(CO)_3L]$	SR (54)	1.55 (6.2); 1.37 (6.1)	4.01 (6.2; 8.8); 3.79 (6.1; 8.8)	6.61	8.7 (5); 7.7 (7); 7.6 (6; 7); 7.5 (5; 7)
	RR (41)	1.41 (6.1); 1.34 (6.1)	4.43 (6.1; 9.0); 4.04 (6.1; 9.0)	6.13	8.7 (5); 8.1 (7); 7.6 (6; 7); 7.5 (5; 7)
	RS (4)	1.49 (6.3); 1.30 (5.8)	4.23; 3.86	6.73	
	SS (1)	1.60 (6.2)		5.94	
$[ReI(CO)_3L]$	SR (52)	1.53 (6.1); 1.38 (6.1)	4.00 (6.1; 8.6); 3.79 (6.1; 8.6)	6.55	8.76 (5.3); 7.96 (7.7); 7.60 (7.7; 8); 7.49 (8; 5.3)
	RR (44)	1.39 (6.1); 1.36 (6.1)	4.45 (6.1; 8.8); 4.05 (6.1; 8.8)	6.07	8.81 (5.1); 7.98 (7.7); 7.6 (7.7; 8); 7.46 (8; 5.1)
	RS (4)	1.47 (6.3); 1.30 (5.9)	4.20; 3.89	6.65	
	SS (< 0.5)	1.59 (6.3)		~ 5.96[e]	

[a] Spectra recorded in $(CDCl_2)_2$ at 303 K; chemical shifts quoted in ppm relative to tetramethylsilane as an internal standard (see Figure 2 for labelling of diastereoisomers); $^3J_{HH}$/Hz given in parentheses; not all signals due to the RR and SS diastereoisomers observed.

[b] Populations (%) given in parentheses

[c] Approximate values only for complexes because of extensive overlap of the signals (see text).

[d] Recorded in $CDCl_3$ solution.

[e] Overlaps with the solvent signal.

Table 3. Kinetic data[a] for the complexes $[ReX(CO)_3L]$.

Temperature/K	$[ReCl(CO)_3L]$			$[ReBr(CO)_3L]$			$[ReI(CO)_3L]$ [b]	
	SR ⇆ SS	RR ⇆ RS		SR ⇆ SS	RR ⇆ RS		RR ⇆ RS	
323[c]	0.05	0.16		0.05	0.09		0.09	
328[c]	0.10	0.27		0.09	0.14		0.18	
333	0.19	0.40		0.15	0.19		0.27	
338	0.30	0.70		0.23	0.32		0.44	
343	0.60	1.10		0.37	0.50		0.63	
348	1.00	1.70		0.61	0.79		0.85	
353	1.70	2.65		0.90	1.10		1.40	
358	2.60	3.60		1.40	1.70		2.20	
363	3.90	5.60		2.10	2.50		3.30	
373	11.2	12.4	0.40[d]	4.80	5.20	2.0[d]	7.10	
383	17.8	18.0	1.00[d]	10.0	10.5	6.5[d]	14.5	1.50[d]
393	28.0	26.0	1.80[d]	20.0	20.3	12.5[d]	28.5	3.50[d]

[a] First order rate constants (s^{-1}) for the major → minor diastereoisomerisations; data from standard band shape analysis except [c].

[b] Independent rates for the SR ⇆ SS diastereoisomerisation not measured (see text).

[c] Data from selective inversion experiments.

[d] Data refer to the reversible ligand dissociation process (see text).

Table 4. Eyring activation parameters[a] for the complexes $[ReX(CO)^3L]$.

Complex	Process	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}	$\Delta G^{\ddagger}$/kJ mol^{-1}
$[ReCl(CO)_3L]$	SR ⇆ SS	104.0 (1.0)	52.0 (3.0)	88.4 (0.1)
	RR ⇆ RS	84.0 (0.6)	-1.0 (2.0)	84.20 (0.01)
	Ligand dissociation[b]	176		113
$[ReBr(CO)_3L]$	SR ⇆ SS	85.8 (0.5)	-4.0 (1.0)	87.0 (0.1)
	RR ⇆ RS	79.8 (0.7)	-19.0 (2.0)	85.5 (0.1)
	Ligand dissociation[b]	108		93
$[ReI(CO)_3L]$[c]	RR ⇆ RS	82.0 (1.0)	-10.0 (3.0)	85.2 (0.1)
	Ligand dissociation[b]	103		95

[a] $\Delta G^{\ddagger}$ quoted at 298 K; errors given in parentheses; data refer to the major → minor diastereoisomerisations.

[b] Approximate values; estimated errors *ca.* ± 10%; $\Delta S^{\ddagger}$ not calculated (considered unreliable due to narrow temperature range).

[c] Activation parameters for the SR ⇆ SS diastereoisomerisation not calculated (see text).

Figure Legends

Figure 1. Fluxional complexes of the C_2-symmetric non-racemic chiral ligands, 2,6-bis[(4S)-alkyloxazolin-2-yl]pyridine (alkyl = methyl or isopropyl), studied previously. The chirality at the carbon atoms enables the mechanisms of the fluxional processes to be determined unambiguously.

Figure 2. The four diastereoisomers of the complexes $[ReX(CO)_3L]$, showing the interconversion pathways resulting from the acetal 'ring flip' process. The letters R and S refer to the configuration at the metal and at the acetal carbon atom, respectively. The acetal-carbon atom is labelled $C_1$and the acetal carbon-H is labelled H_A.

Figure 3. 300 MHz ^1H NMR spectrum of $[ReBr(CO)_3L]$ in $(CDCl_2)_2$, showing the acetal ring methyl and acetal carbon-H regions. See Figure 2 for labelling. The broad signal denoted * is probably due to water.

Figure 4. Spectra show the selective inversion of the RR diastereoisomer of the complex $[ReBr(CO)_3L]$ at 323 K. Delay times are shown alongside. The observed signal (RS diastereoisomer) is donated *.

Figure 5. Experimental and computer simulated variable temperature ^1H NMR spectra of the complex $[ReBr(CO)_3L]$. Rate constants are reported in Table 4. The bands denoted * and ♦ are due to solvent and free ligand, respectively.

Figure 6. Two possible mechanisms for the acetal ring flip in the complexes $[ReX(CO)_3L]$.