

1-1-2003

Tricarbonylrhenium(I) halide complexes of chiral non-racemic 2-(dioxolanyl)-(dioxanyl)pyridine ligands: synthesis, NMR and DFT calculations.

Peter J. Heard

Glyndwr University, p.heard@glyndwr.ac.uk

Paul M. King

Phunrawie Sroisuwana

Nikolas Kaltsoyannis

Follow this and additional works at: <http://epubs.glyndwr.ac.uk/chem>

 Part of the [Inorganic Chemistry Commons](#), [Organic Chemistry Commons](#), and the [Physical Chemistry Commons](#)

This is the author's final version of the work after peer review. This article was originally published in the *Polyhedron Journal* in 2003 by Elsevier. The published article can be found at

<http://www.sciencedirect.com>

Recommended Citation

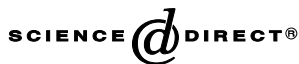
Heard, P. J., King, P. M., Sroisuwana, P., & Kaltsoyannis, N. (2003) 'Tricarbonylrhenium(I) halide complexes of chiral non-racemic 2-(dioxolanyl)-(dioxanyl)pyridine ligands: synthesis, NMR and DFT calculations'. *Polyhedron*, 22 (25-26), 3371-3378

This Article is brought to you for free and open access by the Materials Science at Glyndŵr University Research Online. It has been accepted for inclusion in Chemistry by an authorized administrator of Glyndŵr University Research Online. For more information, please contact d.jepson@glyndwr.ac.uk.



PERGAMON

Available online at www.sciencedirect.com



Polyhedron xxx (2003) xxx–xxx



POLYHEDRON

www.elsevier.com/locate/poly

Tricarbonylrhenium(I) halide complexes of chiral non-racemic 2-(dioxolanyl)-6-(dioxanyl)pyridine ligands: synthesis, NMR and DFT calculations

Peter J. Heard^{a,*}, Paul M. King^a, Phunrawie Sroisuwana^a, Nikolas Kaltsoyannis^b^a School of Biological and Chemical Sciences, Birkbeck University of London, Malet Street, London WC1E 7HX, UK^b Department of Chemistry, University College London, Christopher Ingold Laboratories, 20 Gordon Street, London WC1H 0AJ, UK

Received 2 June 2003; accepted 13 August 2003

Abstract

The chiral non-racemic O/N/O donor ligands 2-[(4*R*,5*R*)-4,5-dimethyl-1,3-dioxolan-2-yl]-6-[(4*R*,6*R*)-4,6-dimethyl-1,3-dioxan-2-yl]pyridine and 2-[(4*R*,5*R*)-4,5-dimethyl-1,3-dioxolan-2-deuteryl]-6-[(4*R*,6*R*)-4,6-dimethyl-1,3-dioxan-2-yl]pyridine were prepared in a stepwise fashion from 2,6-dibromopyridine. Reaction with the pentacarbonylhalogenorhenium(I) compounds yields the complexes [ReX(CO)₃L], in which the ligands act in a N/O bidentate chelate fashion. There are eight possible diastereoisomers, three of which are observable in solution. DFT calculations indicate that the relative stability of the diastereoisomers is SR⁵ > RR⁵ > SS⁵ ≈ RS⁵ > RS⁶ > SS⁶ > RR⁶ > SR⁶. Above ambient temperature, a dynamic process leads to the exchange of 2 of the 3 diastereoisomers: the free energy of activation is ca. 79 kJ mol⁻¹. The results of the DFT calculations and the magnitude of Δ*G*[‡] suggest the dynamic process to be the *flip* of the co-ordinated acetal ring.

© 2003 Published by Elsevier Ltd.

Keywords: 6-Bromopyridine-2-aldehyde; Tricarbonylrhenium(I) halide complexes; Diastereoisomers; ¹H NMR

1. Introduction

Chiral non-racemic C₂-symmetric N/N/N tridentate ligands, such as 2,6-bis(oxazolanyl)pyridines have been used extensively as auxiliary ligands in both stoichiometric and catalytic transition metal-mediated enantioselective organic transformations [1]. When such ligands are restricted to a bidentate bonding mode, the ligands undergo a dynamic stereochemical rearrangement that leads to the exchange of co-ordinated and pendant donor groups [2,3]. The chiral centres on the ligands provide an excellent spectroscopic handle on the stereodynamics, allowing the fluxional pathway to be determined unambiguously.

Recently, as part of our ongoing researches on fluxionality in 'chiral-at-ligand' organo-transition metal

complexes, we reported on the tricarbonylhalogenorhenium(I) complexes of the O/N/O hybrid ligands 2,6-bis[(4*R*,5*R*)-4,5-dimethyl-1,3-dioxolan-2-yl]pyridine (L¹) [4] and 2,6-bis[(4*R*,6*R*)-4,6-dimethyl-1,3-dioxan-2-yl]pyridine (L²) [5] (Fig. 1). These complexes undergo three dynamic processes; namely a flip of the co-ordinated acetal ring and exchange of the co-ordinated and pendant acetal rings via tick-tock and rotation mechanisms [4,5]. The size of the acetal ring [five-membered (dioxolanyl) or six-membered (dioxanyl)] has opposite effects on the relative energies of ring flip and tick-tock processes: Δ*G*[‡] for the ring flip process is lowered on substitution of L¹ for L², while that for the tick-tock exchange increases. The reasons for this were not obvious and we therefore chose to investigate the analogous complexes of the mixed acetal ligand 2-[(4*R*,5*R*)-4,5-dimethyl-1,3-dioxolan-2-yl]-6-[(4*R*,6*R*)-4,6-dimethyl-1,3-dioxan-2-yl]pyridine (L^{HH}) in an attempt to gain further insights on the problem. The results of this study are reported here.

* Corresponding author. Tel.: +44-20-7679-7480; fax: +40-20-7679-7464.

E-mail address: p.heard@bbk.ac.uk (P.J. Heard).

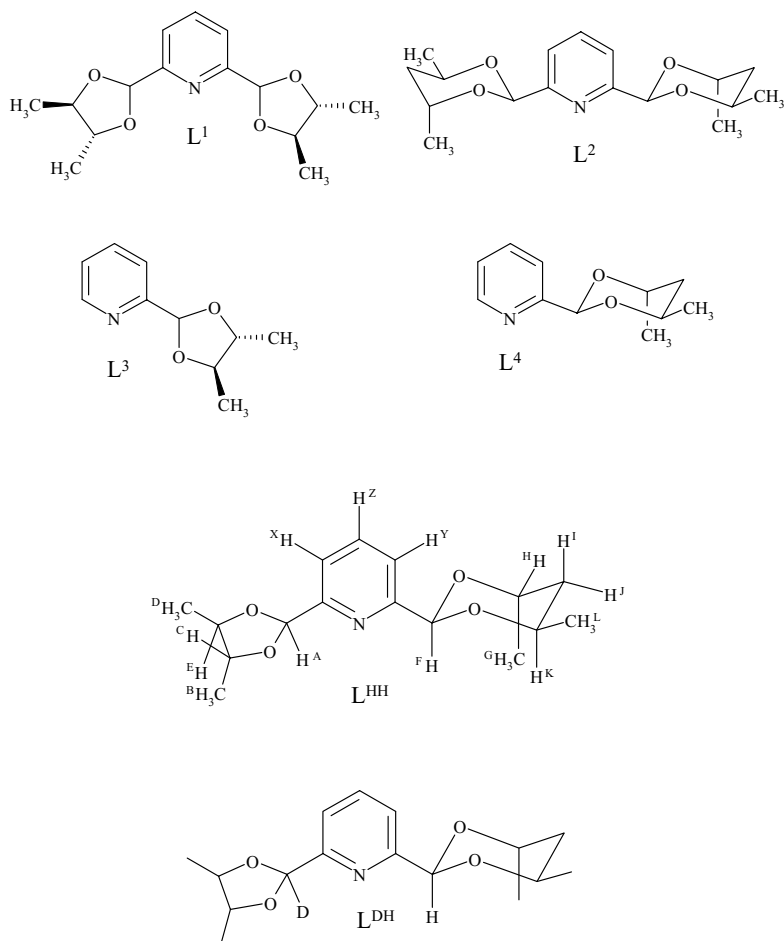


Fig. 1. The chiral non-racemic ligands L^1 , L^2 , L^3 , L^4 , L^{HH} and L^{HD} , showing the hydrogen atom labelling for L^{HH} .

55 2. Results

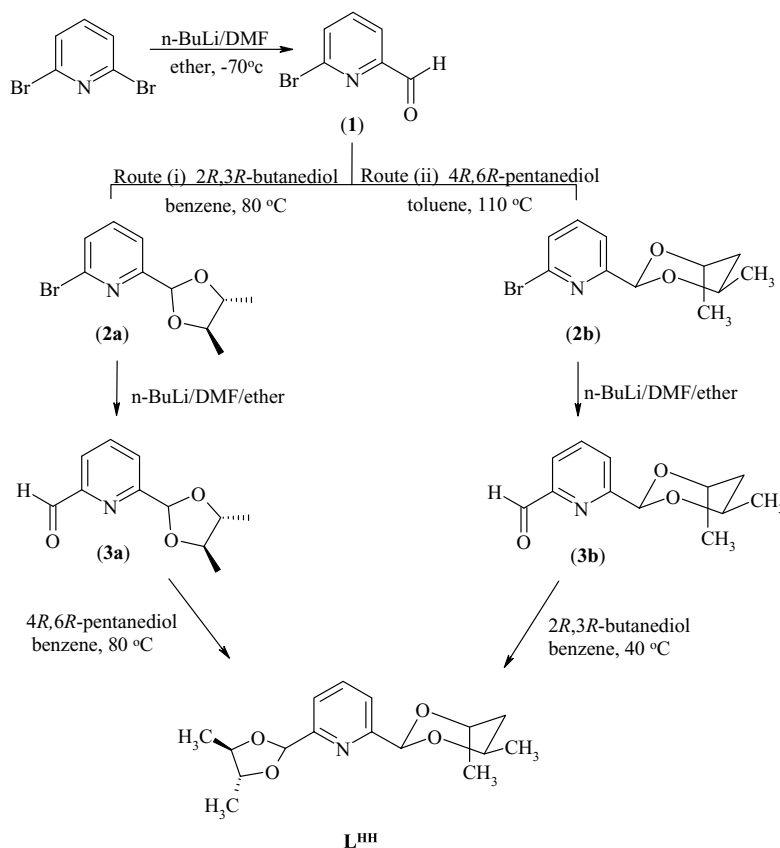
56 2.1. The ligands

57 2-[(4*R*,5*R*)-4,5-dimethyl-1,3-dioxolan-2-yl]-6-[(4*R*,6*R*)-
58 4,6-dimethyl-1,3-dioxan-2-yl]pyridine (L^{HH}) was syn-
59 thesised from 2,6-dibromopyridine, as shown in Scheme
60 1, and characterised by mass spectrometry and NMR:
61 data are reported in Tables 1 and 2. Both routes give
62 similar overall yields. During the work-up of (**3a/3b**), the
63 attached acetal ring can be cleaved by hydrochloric acid,
64 used in the work-up, yielding a small amount of 2,6-
65 pyridinedicarboxaldehyde. Route (i) is thus the pre-
66 ferred pathway: (2*R*,3*R*)-butane-2,3-diol is the cheaper
67 of the diols.

68 The ^1H NMR spectrum of L^{HH} is fully and unam-
69 biguously assignable. The acetal-C hydrogens, H_A (di-
70 oxolanyl) and H_F (dioxanyl) (see Fig. 1 for hydrogen
71 atom labelling), are identified by their low frequency
72 shifts (ca. δ 6.0) and differentiated by a NOESY exper-
73 iment. H_A undergoes cross-relaxation with Me_B and
74 H_E , which are assigned to the dioxolanyl ring on the
75 basis of their scalar couplings, while H_F undergoes

cross-relaxation with H_L and Me_G , of the dioxanyl 76
ring. The NOEs observed between H_F and H_L , and H_F 77
and Me_G are consistent with the dioxanyl ring adopting 78
a chair configuration with the pyridine ring equatorial. 79
The full $\text{AB}_3\text{CD}_3\text{E}$ and $\text{AB}_3\text{CDEFG}_3$ spin systems of the 80
dioxolanyl and dioxanyl rings were analysed (non- 81
iteratively) using the program GNMR [6]. The 3- and 5- 82
position hydrogens of the pyridine ring, H_X and H_Z , 83
are distinguished by virtue of the fact that they undergo 84
cross-relaxation with the acetal-C hydrogens, H_A and 85
 H_F , respectively. The ^{13}C NMR spectrum was assigned 86
on the basis of signal chemical shifts, DEPT experi- 87
ments and by comparison with the spectra obtained [7] 88
for L^1 , L^2 , 2-[(4*R*,5*R*)-4,5-dimethyl-1,3-dioxolan-2- 89
yl]pyridine (L^3) [8] and 2-[(4*R*,6*R*)-4,6-dimethyl-1,3-di- 90
oxan-2-yl] pyridine (L^4) [5]. NMR data are reported in 91
Table 2. 92

The deuterium labelled analogues of L^{HH} , namely 2- 93
[(4*R*,5*R*)-4,5-dimethyl-1,3-dioxolan-2-deuteryl]-6-[(4*R*,6*R*)- 94
-4,6-dimethyl-1,3-dioxan-2-yl]pyridine (L^{DH}) and 2-[(4*R*, 95
5*R*)-4,5-dimethyl-1,3-dioxolan-2-deuteryl]-6-[(4*R*,6*R*)-4,6- 96
dimethyl-1,3-dioxan-2-deuteryl]pyridine (L^{DD}) were 97
prepared similarly, using d_7 -dimethylformamide in the 98



Scheme 1.

99 appropriate step(s) (Scheme 1), and identified by mass
100 spectrometry and NMR: data are reported in Tables 1
101 and 2. The selective deuteration of the dioxolanyl ring
102 (synthesis of L^{DH}) is best achieved by reaction of 2-
103 deuterated aldehyde-6-[(4*R*,6*R*)-4,6-dimethyl-1,3-dioxan-2-
104 deuteryl]pyridine with (2*R*,3*R*)-butane-2,3-diol [i.e.,

route (ii), Scheme 1]. This route gives the best overall 105
yield of L^{DH} and minimises the amount of 2-[(4*R*,5*R*)- 106
4,5-dimethyl-1,3-dioxolan-2-yl]-6-[(4*R*,6*R*)-4,6-dimethyl- 107
1,3-dioxan-2-deuteryl]pyridine (L^{HD}), which is produced 108
as a side product: careful control of the reaction con- 109
ditions enabled L^{DH} to be isolated in 80% excess over 110

Table 1

Analytical data for L^{HH} , L^{DH} and L^{DD} , and the complexes $[\text{ReX}(\text{CO})_3(\text{L})]$ ($\text{L} = L^{HH}$, $\text{X} = \text{Cl}$, Br or I) and $[\text{ReBr}(\text{CO})_3(L^{HD})]$

Ligand/Complex	Reaction time (h)	Yield (%)	$\nu(\text{CO})^a$ (cm^{-1})	Mass spectral data	Analyses ^b (%)		
					C	H	N
L^{HH}				316 $[\text{M} + \text{Na}]^+$ 294 $[\text{M} + \text{H}]^+$			
L^{DH}				317 $[\text{M} + \text{Na}]^+$ 295 $[\text{M} + \text{H}]^+$			
L^{DD}				318 $[\text{M} + \text{Na}]^+$ 296 $[\text{M} + \text{H}]^+$			
$[\text{ReCl}(\text{CO})_3(L^{HH})]$	24	79	1904; 1917; 2031	599 $[\text{M}]^+$ 564 $[\text{M} - \text{Cl}]^+$	37.24 (38.09)	3.72 (3.87)	2.18 (2.34)
$[\text{ReBr}(\text{CO})_3(L^{HH})]$	72	62	1905; 1919; 2031	643 $[\text{M}]^+$ 564 $[\text{M} - \text{Br}]^+$	36.65 (35.46)	3.64 (3.60)	2.39 (2.18)
$[\text{ReI}(\text{CO})_3(L^{HH})]$	96	68	1909; 1920; 2031	691 $[\text{M}]^+$ 564 $[\text{M} - \text{I}]^+$	34.57 (33.05)	3.53 (3.36)	2.32 (2.03)
$[\text{ReBr}(\text{CO})_3(L^{DH})]$	72	51	1906; 1919; 2031	644 $[\text{M}]^+$ 565 $[\text{M} - \text{Br}]^+$	32.94 (35.41)	3.41 (3.44)	1.85 (2.17)

Yield reported relative to the $[\text{ReX}(\text{CO})_3]$ compounds.^a Infrared data. Spectra recorded in CH_2Cl_2 solution.^b Calculated values in parentheses. Poor analytical figures due to impurities, which could not be separated (see text).

Table 2
NMR data^a L^{HH}

Assignment ^b	¹ H NMR data		Assignment	¹³ C NMR data
	δ	Scalar couplings (Hz)		δ
H _A	6.01 (6.0) ^b		CH ₃	16.9
H _B	1.34	J_{BC} 6.1; J_{BE} 0.1	CH ₃	17.0
H _C	3.80	J_{CD} 0.1; J_{CE} 7.6	CH ₃	17.3
H _D	1.38	J_{DE} 6.1	CH ₃	21.9
H _E	3.84		CH ₂	36.8
H _F	5.95 (5.9) ^c		CHCH ₃ (dioxanyl ring)	68.1
H _G	1.50	J_{GH} 6.9	CHCH ₃ (dioxanyl ring)	68.8
H _H	4.49	J_{HI} 6.1; J_{HI} 1.0	CHCH ₃ (dioxolanyl ring)	78.8
H _I	2.02	J_{IJ} 13.3; J_{IK} 11.7	CHCH ₃ (dioxolanyl ring)	80.4
H _J	1.45	J_{JK} 2.4	acetal-C (dioxanyl ring)	94.8 (25) ^d
H _K	4.24	J_{KL} 6.2	acetal-C (dioxolanyl ring)	102.0 (25) ^e
H _L	1.27		pyridine-C	120.3; 121.2; 137.7; 156.7 ^f ; 157.3 ^f
H _X	7.79			
H _Y	7.66	J_{XY} 7.8; J_{XZ} 7.7		
H _Z	7.58	J_{YZ} 1.1		

^a Recorded in CDCl₃ at 298 K; chemical shifts quoted relative to trimethylsilane. See Fig. 1 for assignments.

^b δ ²H for L^{DH}/L^{DD} given in parentheses.

^c δ ²H L^{DD} given in parentheses.

^d ¹ J_{CD} /Hz for L^{DH}/L^{DD} given in parentheses.

^e ¹ J_{CD} /Hz for L^{DD} given in parentheses.

^f Quaternary carbon.

111 L^{HD}. Attempts to prepare L^{HD} were less successful: L^{HD}
112 could not be prepared cleanly.

113 2.2. Complexes

114 The complexes, [ReX(CO)₃L] (L = L^{HH}, X = Cl, Br
115 or I; L = L^{DH}, X = Br) were prepared by refluxing the
116 [ReX(CO)₅] compounds with a small excess of the ap-
117 propriate ligand in chloroform. The complexes were
118 isolated as air-stable, microcrystalline solids, soluble in
119 common organic solvents. The infrared spectra of the
120 complexes each displayed three bands in the carbonyl
121 stretching region, characteristic of a *fac*-octahedral co-
122 ordination geometry for the [Re(CO)₃] moiety [9], indi-
123 cating the potentially terdentate ligands are binding in
124 the expected N/O bidentate fashion. The FAB mass
125 spectra of the complexes each display low intensity
126 peaks due to the molecular ions, [M]⁺, and high inten-
127 sity peaks due to the species [M – halogen]⁺. The poor
128 analytical figures obtained, particularly for [Re-
129 Br(CO)₃L^{DH}], result from the presence of impurities,
130 which are evidenced in the NMR spectra. Analytical
131 data are reported in Table 1.

132 Assuming that inversion of configuration at the co-
133 ordinated oxygen atom is rapid [10], the [ReX(CO)₃L]
134 (L = L^{HH} or L^{DH}) complexes possess six chiral cen-
135 tres: the 4- and 5-positions of the dioxolanyl ring, the
136 4- and 6-positions of the dioxanyl ring, the acetal-
137 carbon atom of co-ordinated acetal ring, and the
138 metal centre. The configuration at 4- and 5-, and 4-
139 and 6-acetal ring positions are fixed (R), but the

140 configurations at the acetal-carbon and the metal can
141 be R or S. Thus, there are eight possible diastereoi-
142 somers, namely RR⁵, RS⁵, SR⁵, SS⁵, RR⁶, RS⁶, SR⁶
143 and SS⁶, depending on the configuration at the metal
144 and at the co-ordinated acetal-carbon, respectively.
145 The numbers refer to which acetal ring [dioxolanyl (5)
146 or dioxanyl (6)] is co-ordinated (Fig. 2). The config-
147 uration at the metal is defined by viewing the metal
148 down the pseudo C₃ axis of symmetry, with the three
149 CO groups down, and assigning priorities to the three
150 remaining ligands according to the Cahn–Ingold–
151 Prelog system [11].

152 The ambient temperature solution ¹H NMR spectra
153 of the [ReX(CO)₃L^{HH}] complexes are highly complex
154 due to the overlapping sub-spectra of at least 3 of the 8
155 possible diastereoisomers (although exchange is slow
156 on the NMR time scale, the diastereoisomers inter-
157 convert in solution, frustrating attempts to separate
158 them [4,5,8]). The acetal-CH region, which is most
159 amenable to analysis, displays three pairs of singlets;
160 each diastereoisomer gives rise to two acetal-CH sig-
161 nals. Additional weak signals that may be due to the
162 presence of minor diastereoisomers or impurities are
163 also observed. The intensities of these additional sig-
164 nals vary, depending on the reaction conditions and the
165 method of purification, suggesting they are more likely
166 to be due to impurities. The assignment of the acetal-
167 CH signals to the dioxolanyl and dioxanyl rings was
168 done on the basis of their spin–lattice relaxation times.
169 Extensive T₁ measurements [7] on ligands L¹–L⁴ and
170 their tricarbonylhalogenorhenium(I) complexes indicate

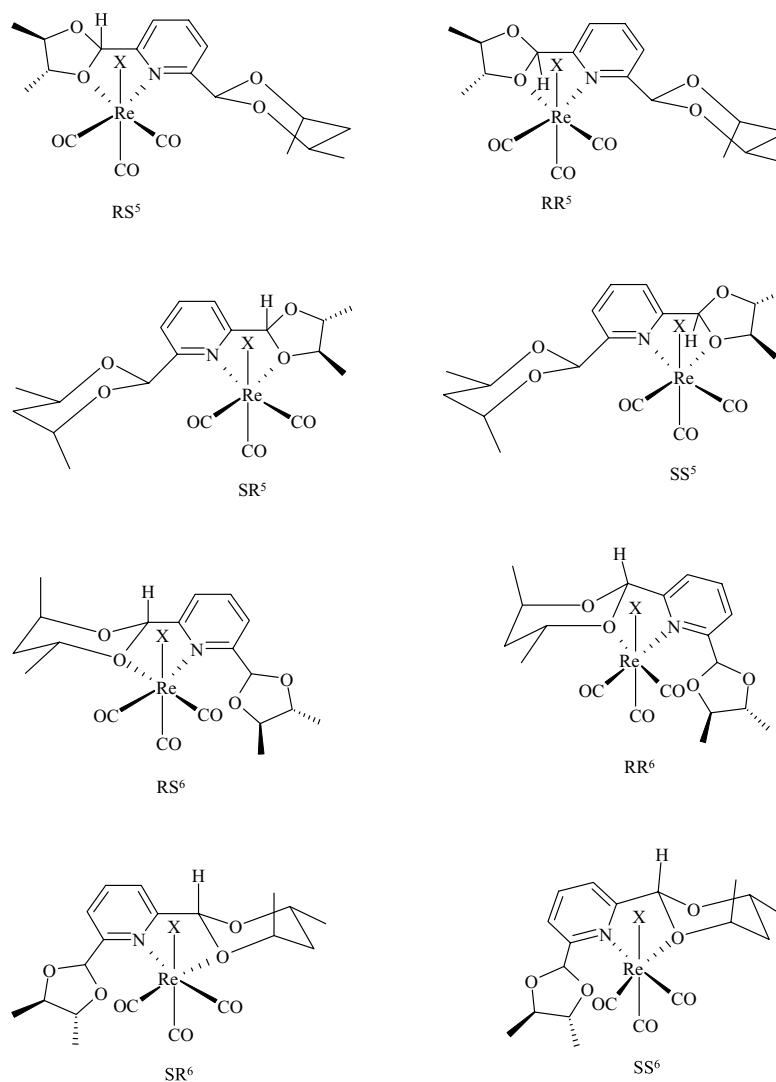


Fig. 2. The eight possible diastereoisomers of the complexes $[\text{ReX}(\text{CO})_3\text{L}]$ $\text{X} = \text{Cl}, \text{Br}$ or I ; $\text{L} = \text{L}^{\text{HH}}$ or L^{DH} . Letters refer to the configuration at the metal and at the acetal-carbon atom of the co-ordinated ring.

171 that the relaxation times for the dioxolanyl-CH's are
172 between ca. 2.4 and 3.2 s, while those for the dioxanyl-
173 CH are between ca. 1.0 and 1.5 s; as might be expected,
174 the relaxation times in the free ligands are generally
175 longer than those in the complexed ligands. The re-
176 laxation times of H_A (dioxolanyl) and H_F (dioxanyl) of
177 free L^{HH} are ca. 2.5 and 1.0 s, respectively. The pairs of
178 acetal-CH signals in the $[\text{ReX}(\text{CO})_3\text{L}^{\text{HH}}]$ complexes
179 also possess T_1 values of ca. 2.5 and 1.0 s (Table 3) and
180 are thus assigned to the dioxolanyl and dioxanyl rings,
181 respectively. The ^1H NMR spectrum of $[\text{Re}-$
182 $\text{Br}(\text{CO})_3\text{L}^{\text{DH}}]$ confirms the assignment. The sub-spectra
183 due to the acetal-ring- and pyridine-hydrogens are also
184 consistent with the presence of three main diastereoi-
185 somers, but the extensive overlap of signals frustrated
186 attempts to analyse the spectra fully in these regions.
187 ^1H NMR data for the acetal-C hydrogens are reported
188 in Table 3.

It is not possible to determine which of the eight
possible diastereoisomers are observed in solution from
the NMR spectra. Quantum chemical (DFT) calcula-
tions (Table 4) show clearly that co-ordination of the
dioxolanyl ring is favoured strongly over the dioxanyl
ring. The relative stabilities of the diastereoisomers are
in the order $\text{SR}^5 > \text{RR}^5 > \text{SS}^5 \approx \text{RS}^5 > \text{RS}^6 > \text{SS}^6 >$
 $\text{RR}^6 > \text{SR}^6$, suggesting that the three solution-state
species are SR^5 , RR^5 and either SS^5 or RS^5 . This is in
accord with trends observed previously in the complexes
 $[\text{ReX}(\text{CO})_3\text{L}^1]$ ($\text{SR} > \text{RR} > \text{SS} > \text{RS}$) [4] and $[\text{Re}-$
 $\text{X}(\text{CO})_3\text{L}^3]$ ($\text{SR} > \text{RR} > \text{RS} > \text{SS}$) [8]. The reasons for
the calculated trend are not obvious; however, the
amount by which the ligand is destabilised on binding
appears to at least play a role. Single point energy cal-
culations were performed on the ligand in each of its
bound geometries (the geometry being that taken from
the DFT optimisations) and compared to that of the free

Table 3

¹H NMR data^a for the [ReX(CO)₃(L)] (L = L^{HH}, X = Cl, Br or I; L = L^{DH}, X = Br) complexes

Compound	Diastereoisomer ^b	$\delta(\text{acetal-CH})^c$	
		H _A	H _F
[ReCl(CO) ₃ (L ^{HH})]	A (60)	6.37 (2.6)	6.55 (1.1)
	B (34)	6.81 (2.4)	6.45 (1.2)
	C (6)	6.62 ^f	6.10 (1.2)
[ReBr(CO) ₃ (L ^{HH})]	A (54)	6.37 (2.6)	6.51 (1.0)
	B (43)	6.83 (2.4)	6.43 (1.2)
	C (3)	6.57 ^d	6.08 (1.2)
[ReI(CO) ₃ (L ^{HH})]	A (64)	6.34 (2.4)	6.40 (1.0)
	B (26)	6.76 (2.4)	6.38 (1.2)
	C (10)	6.57 (2.5)	6.05 (1.2)
[ReBr(CO) ₃ (L ^{DH})]	A (60)		6.51 (1.0)
	B (32)		6.43 (1.2)
	C (8)		6.08 (1.2)

^a Recorded in CDCl₃ solution at 298 K; chemical shifts quoted relative to tetramethylsilane.^b Populations (%) given in parentheses.^c Spin lattice relaxation times, measured at 273 K, given in parentheses.^d T₁ not measured due to overlap signals arising from minor impurities.

Table 4

Calculated energies for the complex [ReCl(CO)₃L^{HH}]

Diastereoisomer ^a	E _{rel} ^b (kJ mol ⁻¹)
SR ⁵	0
RR ⁵	9
SS ⁵	15
RS ⁵	15
RS ⁶	28
SS ⁶	32
RR ⁶	39
SR ⁶	50

^a See Fig. 2 for labelling.^b Relative energy.

ligand. The results (Table 5) indicate that the ligand is destabilised on binding; the amount by which the ligand is destabilised follows the trend SR⁵ < RR⁵ < RS⁵ <

Table 5

Calculated energies for isolated ligand, L^{HH}

Ligand geometry ^a	E _{rel} ^b (kJ mol ⁻¹)
Free ligand	0
SR ⁵	33
RR ⁵	37
RS ⁵	40
SS ⁵	41
RS ⁶	45
SS ⁶	45
RR ⁶	49
SR ⁶	58

^a Labels refer to the diastereoisomer in which a particular geometry occurs (see text). See Fig. 2 for labelling.^b Relative energy.

SS⁵ < RS⁶ ≈ SS⁶ < RR⁶ < SR⁶, close to the trend in the relative energies of the complexes (see above).

On warming, the ¹H NMR signals display reversible band broadening, due to a dynamic process that leads to the interconversion of diastereoisomers (**B**) and (**C**) (see Table 2 for labelling). There are three possible exchange pathways, namely a flip of the co-ordinated acetal ring, the tick-tock exchange of pendant and co-ordinated acetal rings and the rotational exchange of pendant and co-ordinated acetal rings [4,5,8]. Although these pathways are distinguishable by their different effects on the NMR lineshapes in the intermediate exchange regime, the uncertainty in the spectral assignment frustrated a full and unambiguous analysis of the spin problem. The barrier for the exchange process was estimated from selective inversion experiments, and found to be ca. 79 kJ mol⁻¹ (there is no significant halogen dependence). For either the tick-tock or rotation processes to be observed, at least one Re-dioxanyl species would need to be evidenced in the NMR spectrum, which the DFT calculations indicate to be unlikely (see above). The dynamic process was therefore assigned tentatively to the acetal ring flip fluxion: the energy barrier measured is close to that observed for the ring flip fluxion in the analogous complexes of L¹ (Table 6).

Table 6

Summary of fluxional energetics in the complexes [ReX(CO)₃L] (X = Cl, Br or I; L = L¹, L², L³ or L⁴)^a

Halide	ΔG^\ddagger (acetal ring flip) (kJ mol ⁻¹)				ΔG^\ddagger (tick-tock exchange) (kJ mol ⁻¹)			
	[ReX(CO) ₃ L ¹]	[ReX(CO) ₃ L ³]	[ReX(CO) ₃ L ²]	[ReX(CO) ₃ L ⁴]	[ReX(CO) ₃ L ¹]	[ReX(CO) ₃ L ³]	[ReX(CO) ₃ L ²]	[ReX(CO) ₃ L ⁴]
Chloride	77	88	b	82	72	c	79	c
	b	84	b	81	b	c	b	c
Bromide	77	87	b	81	72	c	77	c
	b	86	b	81	b	c	b	c
Iodide	78	85	b	78	73	c	75	c
	b	b	b	81	b	c	b	c

^a Data published in [4,5] and [8].^b Not all fluxional processes are measurable due to the different diastereoisomer populations.^c The tick-tock fluxion does not occur in complexes of L³ or L⁴.

235 **3. Discussion**

236 Table 6 summarises the activation energies for the
237 acetal-ring flip and tick-tock exchange processes in the
238 tricarbonylhalogenorhenium(I) complexes of L^1 – L^4 .
239 Data show that substitution of the dioxolanyl ligands
240 with the dioxanyl ligands has opposite effects on the
241 energy barriers: ΔG^\ddagger (ring flip) decreases, while ΔG^\ddagger
242 (tick-tock) increases. This observation was difficult to
243 rationalise and led to the study reported here. It was
244 believed initially [5] that the ground-state energy was
245 lower in the dioxanyl complexes. The DFT calculations
246 indicate clearly that this is not the case: binding of
247 dioxolanyl ring in $[\text{ReX}(\text{CO})_3\text{L}^{\text{HH}}]$ is favoured by ca.
248 12–50 kJ mol⁻¹. The lower ground state energy in the
249 dioxolanyl complexes presumably accounts for the in-
250 creased barrier to the ring flip process.

251 The lower ground state energy of the dioxolanyl
252 complexes may also be expected to result in an increase
253 in the barrier to the tick-tock exchange fluxion, which is
254 not the case. Thus the decrease in the barrier to the tick-
255 tock exchange fluxion that occurs when L^2 is substituted
256 with L^1 must be the result of a greater stabilisation of
257 the transition state energy. This stabilisation arises
258 presumably because of the more favourable Re-dioxo-
259 lanyl interactions in the transition state, in which the
260 ligand is bound to the metal centre in a pseudo-terden-
261 tate fashion [4,5].

262 **4. Experimental**263 *4.1. Synthetic methods*

264 All procedures were carried out using standard
265 Schlenk techniques under an atmosphere of dry, oxygen-
266 free nitrogen. Solvents were dried by distillation from
267 appropriate drying agents [12] and stored under nitro-
268 gen. Starting materials were purchased from standard
269 sources. The $[\text{ReX}(\text{CO})_5]$ (X = Cl, Br or I) compounds
270 were prepared by previously published procedures [13].

271 The non-racemic chiral acetal ligand 2-[(4*R*,5*R*)-4,5-
272 dimethyl-1,3-dioxolan-2-yl]-6-[(4*R*,6*R*)-4,6-dimethyl-1,3-
273 dioxan-2-yl]pyridine (L^{HH}) was synthesised in a stepwise
274 fashion from 2,6-dibromopyridine, as detailed below.
275 L^{HH} can be prepared via either route (i) or route (ii)
276 (Scheme 1). The former pathway is the economically
277 preferred route because, during preparation of (**3a**) or
278 (**3b**), the acetal group reacts with hydrochloric acid, which
279 is used in the work-up, to yield 2,6-pyridinedicarboxal-
280 dehyde: (4*R*,6*R*)-pentanediol is the more expensive diol.

281 *4.1.1. 6-Bromopyridine-2-aldehyde (1)*

282 6-Bromopyridine-2-aldehyde was prepared using a
283 procedure adapted from that previously published [14].

To a slurry of 10.0 g (0.042 mol) of 2,6-dibromopyridine 284
in 250 cm³ of cold (–80 °C) diethyl ether, 27.0 cm³ of 1.6 285
M of *n*-butyllithium in hexanes was added dropwise. 286
After the addition was complete, the reaction mixture 287
was allowed to warm to –40 °C; a clear yellow solution 288
resulted. This solution was cooled to –80 °C and 7 cm³ 289
(0.084 mol) of *N,N*-dimethylformamide in diethyl ether 290
(20 cm³) was added slowly. The reaction was stirred at 291
–70 °C for 2 h, during which time a white solid pre- 292
cipitated. The mixture was allowed to warm to –10 °C 293
and hydrolysed with 10 cm³ of concentrated hydro- 294
chloric acid. The aqueous phase was separated and ex- 295
tracted with diethyl ether. The extracts and ether phase 296
were combined, washed with water, dried over magne- 297
sium sulfate, and evaporated to dryness. Crystallisation 298
of the solid residue from a diethyl ether/*n*-pentane 299
mixture gave 5.94 g (76%) of pure (**1**). 300

301 *4.1.2. 2-[(4*R*,5*R*)-dimethyl-1,3-dioxolan-2-yl]-6-Bromo- 302
pyridine (2a)*

1 (5.0 g, 0.027 mol), (2*R*,3*R*)-butanediol (2.7 cm³, 303
0.030 mol), 2,2-dimethoxypropane (3.7 cm³, 0.030 mol), 304
and *para*-toluenesulfonic acid (ca. 100 mg) were refluxed 305
for 18 h in 30 cm³ of benzene. The resulting solution was 306
extracted with aqueous sodium carbonate solution 307
(3 × 30 cm³) then water (3 × 30 cm³), dried over mag- 308
nesium sulfate, and concentrated to dryness in vacuo. 309
The solid residue was crystallised from hot hexane, 310
yielding pure (**2a**). Yield: 3.6 g (52%). 311

312 *4.1.3. 2-[(4*R*,5*R*)-dimethyl-1,3-dioxolan-2-yl]-6-Alde- 313
hydepyridine (3a)*

2-[(4*R*,5*R*)-dimethyl-1,3-dioxolan-2-yl]-6-Aldehyde- 314
pyridine was prepared using a similar procedure to that 315
for (**1**). Yield: 38%. 316

317 *4.1.4. 2-[(4*R*,5*R*)-dimethyl-1,3-dioxolan-2-yl]-6-[(4*R*,6*R*)- 318
4,6-dimethyl-1,3-dioxan-2-yl]Pyridine (L^{HH})*

3a (0.80 g, 3.86 mmol), (4*R*,6*R*)-pentanediol (0.41 g, 319
3.90 mmol), 2,2-dimethoxypropane (0.48 cm³, 3.90 320
mmol), and *para*-toluenesulfonic acid (ca. 100 mg) were 321
refluxed for 72 h in 30 cm³ of toluene. The resulting 322
solution was extracted with aqueous sodium carbonate 323
solution (3 × 30 cm³) then water (3 × 30 cm³), dried over 324
magnesium sulfate, and concentrated to dryness in va- 325
cuo. The residue was crystallisation from hot petroleum 326
ether to yield 0.71 g (63%) of L^{HH} . 327

328 *4.2. Physical methods*

¹H, ¹³C and ²H NMR spectra were recorded on a 329
Bruker DRX500 Fourier transform spectrometer oper- 330
ating at 500.13, 125.75 and 76.77 MHz, respectively. 331
Chemical shifts are quoted relative to tetramethylsilane. 332
Probe temperatures were controlled by a standard B-VT 333

334 2000 unit and are considered accurate to ± 1 K. Spin-
335 lattice relaxation times, and COSY and NOESY spectra
336 were obtained using the standard Bruker automation
337 programs T1IR, COSYST and NOESYST, respectively.
338 Selective inversion experiments were carried out using our
339 SOFTPULVD program, which generates the pulse se-
340 quence D1-180°-REBURP55-VD-90°-FID. The relaxa-
341 tion delay was 25 s and the VD list typically contained 20
342 delays. Exchange rates were extracted from the longitu-
343 dinal magnetisations using the program CIFIT [15].

344 Infrared spectra were recorded in CH₂Cl₂ solution on
345 a Shimadzu hyper 8700 FT-IR spectrometer operating
346 in the region 4000–400 cm⁻¹. Fast atom bombardment
347 mass spectra were obtained at the London School of
348 Pharmacy on a VG Analytical ZAB-SE4F instrument,
349 using Xe⁺ bombardment at 8 kV energy, on samples in a
350 matrix of 3-nitrobenzyl alcohol. Elemental analyses
351 were carried out at University College London.

352 4.3. Computations

353 The initial free ligand geometric structure was con-
354 structed using the Molden molecular modelling software
355 [16] using fragments taken from the Cambridge Crysta-
356 llographic Database. A DFT/B3LYP [17] geometry
357 optimisation was performed, without symmetry con-
358 straints (6-31G** basis set), using GAMESS-UK version
359 6.2 [18]. In order to check the conformational stability
360 of the ligands when bound to the metal centre a number
361 of additional calculations were performed. These com-
362 pared the geometry of the bound ligand (see below) to
363 that of the optimised free ligand. Calculations were
364 again performed with GAMESS-UK using a 6-31G**
365 basis-set at the DFT/B3LYP level of theory.

366 Calculations on the complexes were performed using
367 the Amsterdam Density Functional program suite [19–
368 23]. An uncontracted double-zeta Slater-type orbital
369 valence basis set, supplemented with a p function for
370 hydrogen and a d polarisation function for carbon, ni-
371 trogen, oxygen and chlorine (ADF Type III), was em-
372 ployed for the non-metallic elements. For Re, the ADF
373 Type IV basis set, which may be described as triple-zeta
374 without polarisation functions was used. Scalar relativ-
375 istic corrections [24] were included via the ZORA to the
376 Dirac equation [25,26]. The frozen core approximation
377 was employed. The relativistic frozen cores (calculated
378 by the ADF auxiliary program Dirac) used were: carbon
379 (1s), nitrogen (1s), oxygen (1s), chlorine (2p) and re-
380 nium (4f). The local density parameterisation of Vosko
381 et al. [27] was employed, in conjunction with Becke's
382 gradient correction [28] to the exchange part of the po-
383 tential and the correlation correction of Perdew [29].
384 The default integration parameter of 4.0 was used in all
385 calculations. Geometry optimisations were conducted
386 without symmetry constraints, using a gradient conver-
387 gence criterion of 0.005 au/Å.

Acknowledgements

We are grateful to The Royal Thai Government for a
studentship (P.S.) and to Johnson Matthey for the loan
of rhenium.

References

- [1] A.H. Ghosh, P. Mathivanan, J. Cappiello, *Tetrahedron Asym-*
metr. 9 (1998) 1.
- [2] P.J. Heard, C. Jones, *J. Chem. Soc., Dalton Trans.* (1997) 1083.
- [3] P.J. Heard, D.A. Tocher, *J. Chem. Soc., Dalton Trans.* (1998)
2169.
- [4] P.J. Heard, A.D. Bain, P. Hazendonk, D.A. Tocher, *J. Chem.*
Soc., Dalton Trans. (1999) 4495.
- [5] P.J. Heard, P.M. King, D.A. Tocher, *J. Chem. Soc., Dalton*
Trans. (2000) 1769.
- [6] gNMR v4.1.0, Cherwell Scientific Limited, Oxford, 2000.
- [7] P. Sroiswan, PhD Thesis, University of London, 2002.
- [8] P.J. Heard, A.D. Bain, P. Hazendonk, *Can. J. Chem.* 77 (1999)
1707.
- [9] D.A. Edwards, J. Marshalsea, *J. Organomet. Chem.* 131 (1977)
73.
- [10] R.F.W. Bader, J.R. Cheeseman, K.E. Laidig, K.B. Wiberg, C.
Breneman, *J. Am. Chem. Soc.* 112 (1990) 6530.
- [11] E.L. Eliel, S.H. Wilen, *Stereochemistry of Organic Compounds*,
Wiley, New York, 1994.
- [12] D.D. Perrin, W.L.F. Armarego, *Purification of Laboratory*
Chemicals, Pergamon, Oxford, 1988.
- [13] P. Schmidt, W.C. Troglor, F. Basolo, *Inorg. Synth.* 28 (1979) 160.
- [14] J.E. Parks, B.E. Wagner, R.H. Holm, *Inorg. Chem.* 10 (1971)
2472.
- [15] A.D. Bain, J.A. Cramer, *J. Magn. Reson. A* 118 (1996) 21.
- [16] G. Schaftenaar, J.H. Noordik, Molden: a pre- and post-processing
program for molecular and electronic structures, *J. Comput.-*
Aided Mol. Des. 14 (2000) 123.
- [17] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [18] GAMESS-UK version 6.2, CFS Ltd., CCLRC Daresbury
Laboratory, 1999. GAMESS-UK is a package of ab initio
programs by M.F. Guest, J.H. van Lenthe, J. Kendrick, K.
Schoffel and P. Sherwood, with contributions from R.D. Amos,
R.J. Buenker, H.J.J. van Dam, M. Dupuis, N.C. Handy, I.H.
Hillier, P.J. Knowles, V. Bonacic-Koutecky, W. von Niessen,
R.J. Harrison, A.P. Rendell, V.R. Saunders, A.J. Stone and
A.H. de Vries. The package is derived from the original
GAMESS code of M. Dupuis, D. Spangler and J. Wendoloski,
NRCC Software Catalog, vol. 1, Program No. QG01 (GA-
MESS), 1980.
- [19] ADF2000, Department of Theoretical Chemistry, Vrije Universi-
teit, Amsterdam, 2000.
- [20] E.J. Baerends, D.E. Ellis, P. Ros, *Chem. Phys.* 2 (1973) 41.
- [21] L. Versluis, T. Ziegler, *J. Chem. Phys.* 88 (1988) 322.
- [22] G. te Velde, E.J. Baerends, *J. Comp. Phys.* 99 (1992) 84.
- [23] C. Fonseca Guerra, J.G. Snijders, G. te Velde, E.J. Baerends,
Theor. Chem. Acc. 99 (1998) 391.
- [24] N. Kaltsoyannis, *J. Chem. Soc., Dalton Trans.* (1997) 1.
- [25] E. van Lenthe, R. van Leeuwen, E.J. Baerends, J.G. Snijders, *Int.*
J. Quantum Chem. 57 (1996) 281.
- [26] E. van Lenthe, J.G. Snijders, E.J. Baerends, *J. Chem. Phys.* 105
(1996) 6505.
- [27] S.H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* 58 (1980) 1200.
- [28] A.D. Becke, *Phys. Rev. A* 38 (1988) 3098.
- [29] J.P. Perdew, *Phys. Rev. B* 33 (1986) 8822.

388

389
390
391

392

393
394
395
396
397
398
399
400
401
402
403
404
405
406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
421
422
423
424
425
426
427
428
429
430
431
432
433
434
435
436
437
438
439
440
441
442
443
444
445
446
447