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Nuclear magnetic resonance studies of molecular dynamics at below-ambient temperatures and crystal structures *

Andrew Gelling,[a] Keith G. Orrell,[a] Anthony G. Osborne,[a] Vladimir Šik,[a] Michael B. Hursthouse[b] and Simon J. Coles[b]

[a] *Department of Chemistry, The University, Exeter EX4 4QD, UK*
[b] *School of Chemistry and Applied Chemistry, University of Wales, College of Cardiff, Cardiff CF1 3TB, UK*

The octahedral complexes *fac*-[ReX(CO)$_3$L] [L = 6-(pyrazol-1-yl)-2,2′-bipyridine (pbipy), 6-(3,5-dimethylpyrazol-1-yl)-2,2′-bipyridine (dmpbipy) or 6-(4-methylpyrazol-1-yl)-2,2′-bipyridine (mpbipy); X = Cl, Br or I] have been studied by low-temperature NMR spectroscopy and in the first two cases by X-ray crystallography. The pendant pyrazol-1-yl ring is shown to be oriented considerably out of the plane of the adjacent co-ordinated pyridyl ring of the ligand. The crystal structure of [ReBr(CO)$_3$(pbipy)] reveals this angle of orientation to be 36.3 and 48.1° in two crystallographically independent molecules. In solution, restricted rotation of the pendant ring occurs leading to distinct pairs of rotamers at low temperatures. Rotation barriers ($\Delta G^\ddagger$) for the pbipy and mpbipy complexes are in the range 39–51 kJ mol^{-1} and the two rotamers have near-equal solution abundances. Methyl substitution at the 3 and 5 positions of the pyrazol-1-yl ring as in the dmpbipy complexes has a major effect on the orientation of the unco-ordinated pendant ring in the solid state as evidenced by the crystal structure of [ReBr(CO)$_3$(dmpbipy)]. This in turn affects the relative rotamer populations in solution, with one rotamer being very dominant, and the barrier to pendant-ring rotation increases somewhat.

In a series of papers [2–5] we have reported studies on some metal complexes of 2,2′:6′,2″-terpyridine (terpy) in which the ligand was bonding in a bidentate chelate mode. In particular we investigated in detail the molecular dynamics of these complexes in solution and identified the mechanism and energies associated with 1,4 metallotropic shifts and restricted rotations of the pendant pyridyl ring. We have now extended our investigations to the metal complexes formed by a series of terdentate nitrogen ligands analogous to terpy in which one or both of the outer rings are replaced by pyrazoles.[6] In Part 1 we reported[1] on the synthesis and solution fluxionality of complexes of the type *fac*-[ReX(CO)$_3$L] [X = Cl, Br or I; L = 6-(pyrazol-1-yl)-2,2′-bipyridine (pbipy), 6-(3,5-dimethylpyrazol-1-yl)-2,2′-bipyridine (dmpbipy) or 6-(4-methylpyrazol-1-yl)-2,2′-bipyridine (mpbipy)]. We now present details of a low-temperature solution NMR study of these complexes and the crystal structures of [ReBr(CO)$_3$(pbipy)] and [ReBr(CO)$_3$(dmpbipy)].

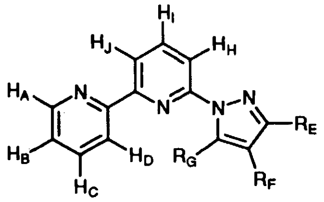
Experimental

Materials

The compounds [ReX(CO)$_3$L] (X = Cl, Br or I; L = pbipy, dmpbipy or mpbipy) were prepared by previous methods.[1]

Physical methods

Hydrogen-1 NMR spectra were recorded on Bruker AM250 or AC300 spectrometers operating at 250.13 or 300.13 MHz respectively. All spectra were recorded in CDCl$_3$ or CD$_2$Cl$_2$ solutions. A standard B-VT 1000 variable-temperature unit was used to control the probe temperature, the calibration of this unit being checked periodically against a Comark digital thermometer. The temperatures are considered accurate to ± 1 °C. Rate data were based on bandshape analysis of ^{1}H NMR spectra using the authors version of the standard DNMR program.[7] Activation parameters based on experimental rate data were calculated using the THERMO program.[8]



	R$_E$	R$_F$	R$_G$
pbipy	H	H	H
mpbipy	H	Me	H
dmpbipy	Me	H	Me

X-Ray structure determinations

[ReBr(CO)$_3$(pbipy)]. *Crystal data.* C$_{16}$H$_{10}$BrN$_4$O$_3$Re, M_r = 572.39, triclinic, space group $P\bar{1}$, a = 9.534(2), b = 13.439(5), c = 14.139(9) Å, α = 74.66(4), β = 79.48(5), γ = 74.20(3)°, U = 1669.1(13) Å^3, Z = 4, D_c = 2.278 Mg m^{-3}, crystal dimensions 0.25 × 0.2 × 0.2 mm, F(000) = 1072, μ = 9.698 mm^{-1}, T = 120(2) K.

Data collection and processing. Data were collected using a FAST TV area-detector diffractometer situated at the window of a rotating-anode generator (50 kV, 45 mA) with a molybdenum target [λ(Mo-Kα) = 0.710 69 Å], following previously described procedures.[9] Somewhat more than one hemisphere of data was recorded, giving a total of 5425 reflections (1.94 < θ < 22.7°) of which 3605 were independent, over index ranges of $-10 < h < 8$, $-13 < k < 14$, $-14 < l < 14$, R_{int} = 0.049 after absorption correction (DIFABS).[10]

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* Rhenium(I) Tricarbonyl Halide Complexes of Pyrazolylbipyridyl Ligands. Part 2.[1]

Table 1 Fractional atomic coordinates (× 10^4) for the two independent molecules of [ReBr(CO)$_3$(pbipy)]

	Molecule 1				Molecule 2		
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Br(1)	3504(1)	1763(1)	1803(1)	Br(2)	660(1)	7273(1)	2671(1)
Re(1)	2186(1)	409(1)	3104(1)	Re(2)	2472(1)	5736(1)	1918(1)
O(1)	3083(8)	928(7)	4865(5)	O(5)	3769(7)	7361(5)	327(5)
O(2)	−572(7)	2241(6)	3191(5)	O(4)	4943(7)	5775(5)	3032(5)
O(3)	681(8)	−1205(6)	4576(5)	O(6)	4739(7)	4095(5)	941(5)
N(1)	4145(8)	−776(6)	2790(6)	N(5)	550(8)	5767(5)	1278(5)
N(2)	1929(8)	31(6)	1717(5)	N(6)	1285(7)	4631(6)	3073(5)
N(3)	−592(8)	846(6)	1685(5)	N(7)	3197(8)	3847(6)	4060(5)
N(4)	−1519(8)	1783(6)	1286(5)	N(8)	3620(8)	4095(6)	4826(5)
C(1)	2753(11)	693(8)	4217(8)	C(18)	3254(10)	6789(8)	900(7)
C(2)	440(11)	1552(8)	3179(6)	C(17)	3998(10)	5740(7)	2627(7)
C(3)	1248(11)	−611(9)	4012(7)	C(19)	3812(10)	4694(8)	1326(6)
C(4)	5178(10)	−1233(8)	3402(7)	C(20)	285(10)	6288(8)	341(7)
C(5)	6461(11)	−1924(9)	3148(8)	C(21)	−1007(10)	6353(8)	−7(8)
C(6)	6685(11)	−2181(8)	2238(8)	C(22)	−2037(10)	5871(8)	611(7)
C(7)	5612(10)	−1733(8)	1621(8)	C(23)	−1770(10)	5338(8)	1535(7)
C(8)	4359(10)	−1043(7)	1911(8)	C(24)	−490(9)	5321(7)	1883(6)
C(9)	3196(10)	−471(7)	1269(7)	C(25)	−142(9)	4797(7)	2889(6)
C(10)	3414(11)	−398(8)	244(7)	C(26)	−1180(10)	4471(8)	3657(7)
C(11)	2293(10)	202(8)	−325(7)	C(27)	−752(10)	3950(7)	4571(7)
C(12)	975(10)	672(8)	151(7)	C(28)	709(10)	3738(8)	4713(6)
C(13)	817(10)	528(7)	1159(6)	C(29)	1689(9)	4108(7)	3933(7)
C(14)	−1274(10)	269(8)	2499(7)	C(32)	4322(10)	3248(8)	3572(7)
C(15)	−2674(10)	850(8)	2634(7)	C(31)	5553(11)	3109(8)	4015(7)
C(16)	−2765(11)	1774(8)	1866(7)	C(30)	5023(10)	3677(8)	4776(7)

Structural analysis and refinement. The structure was solved by heavy-atom methods (SHELXS)[11] to give two independent molecules and then subjected to full-matrix least-squares refinement based on F_o^2 (SHELXL 93).[12] Non-hydrogen atoms were refined anisotropically; hydrogens were included with U_{iso} values fixed at 1.5 U_{eq} of the atom to which each was bonded. The weighting scheme used was $w = 1/[\sigma^2(F_o^2)]$.

Final wR_2* and R_1* values were 0.105 and 0.042 respectively, for all data. The corresponding wR_2 and R_1 values for 3605 data with $F_o > 4\sigma(F_o)$ are 0.0941 and 0.0377 respectively for 471 parameters (ρ_{max}, ρ_{min} 2.73, −1.227 e Å^{-3}).

Diagrams were drawn with SNOOPI.[13] Sources of scattering factors are given in ref. 12.

[ReBr(CO)$_3$(dmpbipy)]. *Crystal data.* $C_{18}H_{14}BrN_4O_3Re$, M_r = 600.4, monoclinic, space group $P2_1/n$, a = 18.9630(10), b = 10.2220(10), c = 22.2850(10) Å, β = 114.00(2)°, U = 3946.2(5) Å^3, Z = 8, D_c = 2.021 Mg m^{-3}, crystal dimensions 0.08 × 0.52 × 0.16mm, $F(000)$ = 2272, μ = 14.643mm^{-1}, T = 298 K.

Data collection and processing. Data were collected using a Siemens R3m/V diffractometer situated at the window of a rotating-anode generator with a copper target [λ(Cu-Kα) = 1.541 78 Å]. The monochromator was a highly oriented graphite crystal. The 2θ scan range was 2.0–110.0° and the scan type was 2θ–θ. Scan speed was variable in the range 1.00–100.00° min^{-1} in x axis. Three standard reflections were measured every 497. A total of 9762 reflections were collected of which 4843 were independent (R_{int} = 0.0323) and 3923 were observed ($F_o > 4\sigma F_o$) over index ranges of $0 < h < 18$, $-10 < k < 10$ and $-23 < l < 21$. The absorption correction was face-indexed numerical and minimum, maximum transmissions were 0.0646 and 0.3562.

Solution and refinement. The structure was solved by heavy-atom methods (SHELXTL PLUS, PC version)[14] to give two independent molecules and then subjected to full-matrix least-squares refinement based on $\Sigma w(F_o - F_c)^2$. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in a riding model with fixed U_{iso} values. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0010F^2$. Number of parameters 488. Final R and wR indices (observed data) were 0.0379 and 0.0488 respectively; corresponding values based on all data were 0.0501 and 0.0563. Goodness-of-fit 0.94. Largest and mean D/r values were 0.012 and 0.002 respectively. Data/parameter ratio 8.0:1; largest difference peak and hole 1.08 and −0.85 e Å^{-3}, respectively.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Results

X-Ray crystallography

In order to confirm the bidentate nature of the pyrazolylbipyridyl ligands in the solid state and to compare the structures with those of complexes involving bidentate terpyridine, the crystal structures of [ReBr(CO)$_3$(pbipy)] and [ReBr(CO)$_3$(dmpbipy)] were determined.

[ReBr(CO)$_3$(pbipy)]. Fractional atomic coordinates are given in Table 1. The crystal structure consists of two virtually equivalent independent molecules, which differ slightly in the orientation of the pendant pyrazol-1-yl rings. A view of the molecules, showing the numbering scheme adopted, is shown in Fig. 1. The molecules display the expected *fac* octahedral co-ordination for Re and the bidentate chelate nature of the pbipy ligand is confirmed, with bonding to the metal through the pyridine nitrogen atoms. Bond distances and angles are listed in Table 2.

The Re–N distances are unequal with Re(1)–N(2) 2.221 and Re(1)–N(1) 2.162 Å in molecule 1 and Re(2)–N(6) 2.261 and Re(2)–N(5) 2.173 Å in molecule 2. This structural feature is also found in compounds involving terpyridine as a bidentate chelate ligand.[2,3,5,15–17] The above values compare with

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* $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$, $R_1 = \Sigma(F_o - F_c)/\Sigma F_o$.

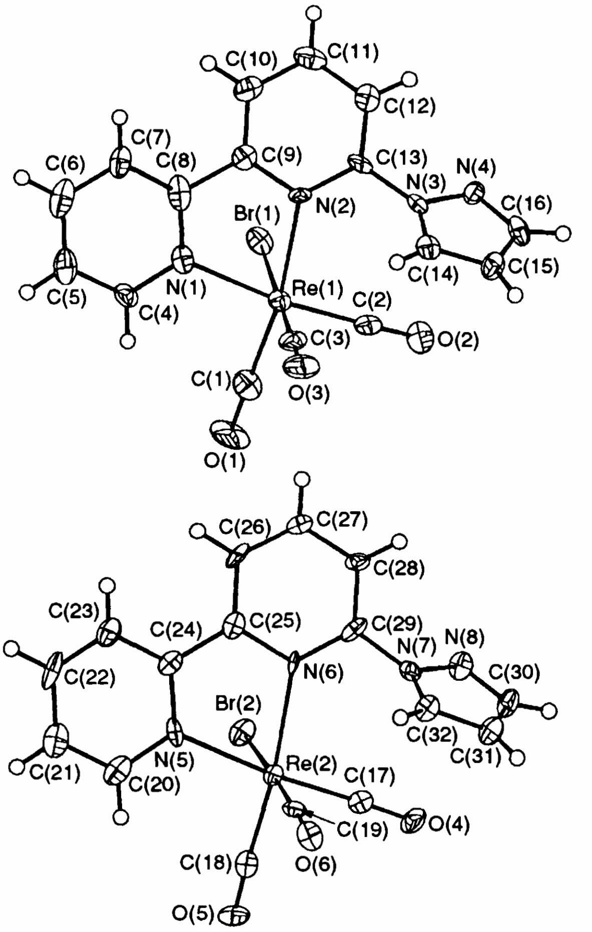

Fig. 1 Structures of the two independent molecules in [ReBr(CO)$_3$-(pbipy)] showing the atomic numbering

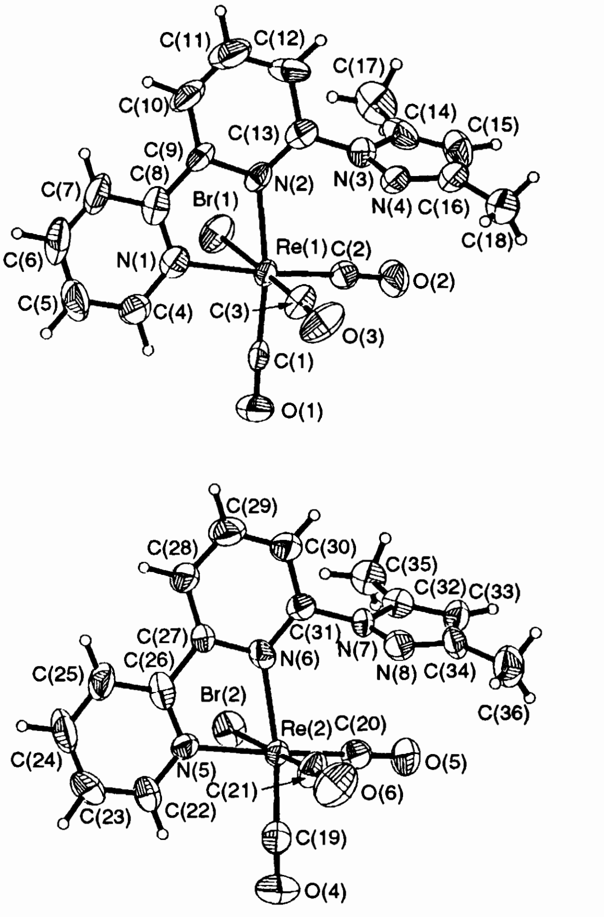

Fig. 2 Structures of the two independent molecules in [ReBr(CO)$_3$-(dmpbipy)] showing the atomic numbering

corresponding values for Re–N of 2.209 and 2.143 Å in [ReBr(CO)$_3$(terpy)].[3]

Inspection of the bond angles at Re (Table 2) shows there to be considerable distortion from regular octahedral geometry. The main distortions arise from the small bite angle of 74.2 or 74.9° of the pbipy ligand and the enlargement of the N–Re–C angle to the carbonyl closest to the pendant pyrazolyl ring. The former values are as expected, virtually identical to the bite angle of terpy (74.3°) in [ReBr(CO)$_3$(terpy)],[3] whereas the latter values of 99.0 and 100.3° compare with an angle of 100.6° for the corresponding angle in the same compound.[3] This variation presumably reflects the differing steric requirements of pyrazole *versus* pyridine as a pendant group.

The dihedral angles between the ring planes of the ligand and particularly the orientation of the pendant ring are of interest. The pyridine rings are inclined to one another at an angle of 15.7 or 11.85° as defined by the torsion angles N(1)–C(8)–C(9)–N(2) and N(5)–C(24)–C(25)–N(6), whereas the orientation of the pendant pyrazole rings relative to the adjacent pyridyl ring can best be described by the torsion angles N(2)–C(13)–N(3)–N(4) 143.7° and N(6)–C(29)–N(7)–N(8) 131.87°. Thus, the angles of orientation are 36.3 and 48.1° in the two crystallographically independent molecules. The nitrogen atoms N(4) and N(8) are directed away from the axial carbonyl group and are *cis* (or proximal) to Br in each molecule. This is in contrast to the structure of [ReBr(CO)$_3$(terpy)] where the corresponding N atom is *trans* (or distal) to bromine.[3]

[ReBr(CO)$_3$(dmpbipy)]. The crystal structure of this complex was investigated as it was suspected, both on the basis of chemical reasoning and from its distinctly different solution NMR properties (see later), that the 3- and 5-methyl substituents on the pyrazol-1-yl ring greatly influence the preferred orientation of the pendant ring.

The structure consists of two virtually equivalent independent molecules {as in the case of [ReBr(CO)$_3$(pbipy)]} which differ somewhat in the orientation of the pendant 3,5-dimethylpyrazol-1-yl rings. A view of the molecules, showing the numbering scheme, is given in Fig. 2. The molecules again display the *fac* octahedral co-ordination for rhenium and the bidentate chelate nature of the pbipy ligand but the pendant ring is oriented quite differently (see later) to the unsubstituted five-membered ring in the pbipy complex.

Fractional atomic coordinates, bond lengths and angles are given in Tables 3 and 4 respectively. The Re–N distances are again somewhat unequal with Re(1)–N(2) 2.195 and Re(1)–N(1) 2.161 Å in molecule 1 and Re(2)–N(6) 2.209 and Re(2)–N(5) 2.147 Å in molecule 2. These values indicate slightly stronger bonding to the peripheral pyridyl nitrogen in keeping with the terpy complexes.[3] Considerable distortion from regular octahedral geometry arises from the small bite angles N(1)–Re(1)–N(2) 74.7° and N(5)–Re(2)–N(6) 75.0° of the dmpbipy ligand. This leads to an opening of the N–Re–C angle to the carbonyl closest to the pendant ring, *viz.* C(2)–Re(1)–N(2) 101.4° (molecule 1) and C(20)–Re(2)–N(6) 102.7° (molecule 2). These angles are significantly larger than in the unsubstituted five-membered ring complex [ReBr(CO)$_3$(pbipy)].

The dihedral angles between the planes of the two pyridyl rings are considerably smaller (*e.g.* 3.6° for molecule 1) than in the pbipy complex where they are in the range 12–16°, but the main difference between the structures of these two complexes lies in the orientation of the pyrazol-1-yl ring. In the dmpbipy complex the preferred solid-state orientation places the methyls pointing outwards from the rhenium centre with the nitrogen atom N(4) or N(8) pointing inwards, in distinct contrast to the

Table 2 Bond lengths (Å) and angles (°) for [ReBr(CO)$_3$(pbipy)]

Molecule 1				Molecule 2			
Br(1)–Re(1)	2.628(2)	N(3)–N(4)	1.373(10)	Br(2)–Re(2)	2.633(2)	N(7)–N(8)	1.368(10)
Re(1)–C(1)	1.912(11)	N(3)–C(13)	1.425(12)	Re(2)–C(18)	1.934(10)	N(7)–C(29)	1.417(11)
Re(1)–C(2)	1.942(10)	N(4)–C(16)	1.316(11)	Re(2)–C(17)	1.913(9)	N(8)–C(30)	1.299(11)
Re(1)–C(3)	1.908(11)	C(4)–C(5)	1.373(14)	Re(2)–C(19)	1.883(11)	C(20)–C(21)	1.381(13)
Re(1)–N(1)	2.162(8)	C(5)–C(6)	1.38(2)	Re(2)–N(5)	2.173(7)	C(21)–C(22)	1.371(13)
Re(1)–N(2)	2.221(7)	C(6)–C(7)	1.372(13)	Re(2)–N(6)	2.261(7)	C(22)–C(23)	1.346(13)
O(1)–C(1)	1.163(11)	C(7)–C(8)	1.369(13)	O(5)–C(18)	1.103(10)	C(23)–C(24)	1.389(12)
O(2)–C(2)	1.143(11)	C(8)–C(9)	1.475(13)	O(4)–C(17)	1.170(10)	C(24)–C(25)	1.465(12)
O(3)–C(3)	1.143(11)	C(9)–C(10)	1.407(13)	O(6)–C(19)	1.181(11)	C(25)–C(26)	1.395(12)
N(1)–C(4)	1.339(11)	C(10)–C(11)	1.393(13)	N(5)–C(20)	1.358(11)	C(26)–C(27)	1.372(12)
N(1)–C(8)	1.349(13)	C(11)–C(12)	1.384(13)	N(5)–C(24)	1.348(11)	C(27)–C(28)	1.385(12)
N(2)–C(9)	1.349(12)	C(12)–C(13)	1.372(12)	N(6)–C(25)	1.379(11)	C(28)–C(29)	1.387(12)
N(2)–C(13)	1.354(11)	C(14)–C(15)	1.358(13)	N(6)–C(29)	1.301(11)	C(31)–C(32)	1.375(13)
N(3)–C(14)	1.371(11)	C(15)–C(16)	1.411(13)	N(7)–C(32)	1.352(12)	C(30)–C(31)	1.422(14)
C(3)–Re(1)–C(1)	87.7(4)	C(16)–N(4)–N(3)	103.8(7)	C(19)–Re(2)–C(18)	87.6(4)	C(30)–N(8)–N(7)	103.9(7)
C(3)–Re(1)–C(2)	92.5(4)	O(1)–C(1)–Re(1)	175.9(9)	C(19)–Re(2)–C(17)	88.4(4)	O(5)–C(18)–Re(2)	176.5(8)
C(1)–Re(1)–C(2)	88.6(4)	O(2)–C(2)–Re(1)	177.7(8)	C(17)–Re(2)–C(18)	84.8(4)	O(4)–C(17)–Re(2)	117.4(7)
C(3)–Re(1)–N(1)	93.3(4)	O(3)–C(3)–Re(1)	178.0(9)	C(19)–Re(2)–N(5)	97.5(3)	O(6)–C(19)–Re(2)	174.2(8)
C(1)–Re(1)–N(1)	97.6(4)	N(1)–C(4)–C(5)	122.4(10)	C(18)–Re(2)–N(5)	99.6(3)	N(5)–C(20)–C(21)	121.6(9)
C(2)–Re(1)–N(1)	171.7(3)	C(4)–C(5)–C(6)	119.0(9)	C(17)–Re(2)–N(5)	172.8(3)	C(22)–C(21)–C(20)	118.9(10)
C(3)–Re(1)–N(2)	97.9(3)	C(7)–C(6)–C(5)	118.6(10)	C(19)–Re(2)–N(6)	97.3(3)	C(23)–C(22)–C(21)	119.8(9)
C(1)–Re(1)–N(2)	170.3(3)	C(8)–C(7)–C(6)	119.9(10)	C(18)–Re(2)–N(6)	173.0(3)	C(22)–C(23)–C(24)	120.3(9)
C(2)–Re(1)–N(2)	99.0(3)	N(1)–C(8)–C(7)	121.8(9)	C(17)–Re(2)–N(6)	100.3(3)	N(5)–C(24)–C(23)	120.5(8)
N(1)–Re(1)–N(2)	74.2(3)	N(1)–C(8)–C(9)	114.6(8)	N(5)–Re(2)–N(6)	74.9(2)	N(5)–C(24)–C(25)	115.7(7)
C(3)–Re(1)–Br(1)	177.7(3)	C(7)–C(8)–C(9)	123.4(10)	C(19)–Re(2)–Br(2)	176.8(3)	C(23)–C(24)–C(25)	123.8(9)
C(1)–Re(1)–Br(1)	94.2(3)	N(2)–C(9)–C(10)	121.6(8)	C(18)–Re(2)–Br(2)	89.2(3)	N(6)–C(25)–C(26)	119.3(8)
C(2)–Re(1)–Br(1)	88.9(3)	N(2)–C(9)–C(8)	115.8(8)	C(17)–Re(2)–Br(2)	91.2(3)	N(6)–C(25)–C(24)	117.6(8)
N(1)–Re(1)–Br(1)	85.2(2)	C(10)–C(9)–C(8)	112.5(9)	N(5)–Re(2)–Br(2)	83.1(2)	C(26)–C(25)–C(24)	123.2(8)
N(2)–Re(1)–Br(1)	80.0(2)	C(11)–C(10)–C(9)	119.4(9)	N(6)–Re(2)–Br(2)	85.9(2)	C(27)–C(26)–C(25)	119.6(8)
C(4)–N(1)–C(8)	118.3(8)	C(12)–C(11)–C(10)	118.3(9)	C(24)–N(5)–C(20)	118.8(7)	C(26)–C(27)–C(28)	119.5(8)
C(4)–N(1)–Re(1)	123.9(7)	C(13)–C(12)–C(11)	119.1(9)	C(20)–N(5)–Re(2)	123.8(6)	C(27)–C(28)–C(29)	118.6(8)
C(8)–N(1)–Re(1)	117.7(6)	N(2)–C(13)–C(12)	123.6(9)	C(24)–N(5)–Re(2)	117.1(5)	N(6)–C(29)–C(28)	122.2(8)
C(9)–N(2)–C(13)	117.7(4)	N(2)–C(13)–N(3)	116.0(7)	C(29)–N(6)–C(25)	120.6(7)	N(6)–C(29)–N(7)	119.0(8)
C(9)–N(2)–Re(1)	113.5(5)	C(12)–C(13)–N(3)	120.3(7)	C(25)–N(6)–Re(2)	110.9(5)	C(28)–C(29)–N(7)	118.7(8)
C(13)–N(2)–Re(1)	125.4(6)	C(15)–C(14)–N(3)	106.2(8)	C(29)–N(6)–Re(2)	126.2(5)	N(7)–C(32)–C(31)	107.0(9)
C(14)–N(3)–N(4)	112.1(7)	C(14)–C(15)–C(16)	105.4(9)	C(32)–N(7)–N(8)	112.3(7)	C(32)–C(31)–C(30)	103.4(9)
C(14)–N(3)–C(13)	128.4(8)	N(4)–C(16)–C(15)	112.5(9)	C(32)–N(7)–C(29)	127.4(8)	N(8)–C(30)–C(31)	113.3(8)
N(4)–N(3)–C(13)	118.8(7)			N(8)–N(7)–C(29)	119.8(7)		

Table 3 Fractional atomic coordinates (× 10^4) for two independent molecules of [ReBr(CO)$_3$(dmpbipy)]

	Molecule 1				Molecule 2		
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re(1)	4 535(1)	2 077(1)	8 353(1)	Re(2)	2 183(1)	2 342(1)	985(1)
Br(1)	3 705(1)	2 863(1)	8 972(1)	Br(2)	1 331(1)	3 083(1)	1 590(1)
O(2)	3 168(5)	2 325(8)	7 012(4)	O(5)	797(5)	2 388(8)	–347(4)
N(3)	4 233(5)	4 892(9)	7 469(4)	N(5)	3 106(5)	2 398(8)	1 947(4)
N(4)	4 550(5)	4 358(8)	7 064(4)	N(7)	1 795(4)	5 106(8)	46(4)
C(2)	3 686(6)	2 257(10)	7 529(5)	N(6)	2 587(4)	4 391(8)	1 121(4)
N(1)	5 460(5)	2 043(9)	9 324(4)	N(8)	2 076(5)	4 521(8)	–373(4)
N(2)	4 972(4)	4 091(8)	8 537(4)	C(26)	3 408(5)	3 559(12)	2 183(5)
O(3)	5 482(5)	1 083(9)	7 630(4)	C(32)	1 076(5)	5 635(10)	–286(5)
C(1)	4 215(6)	324(11)	8 335(4)	C(20)	1 335(6)	2 388(10)	159(5)
C(16)	4 030(8)	4 572(12)	6 464(5)	C(25)	3 968(6)	3 722(12)	2 823(5)
C(9)	5 494(6)	4 351(10)	9 170(5)	C(31)	2 335(5)	5 400(10)	694(5)
O(1)	4 020(5)	–772(8)	8 320(4)	C(33)	872(6)	5 317(10)	–919(5)
C(13)	4 723(6)	5 119(11)	8 129(5)	C(27)	3 112(5)	4 695(10)	1 740(4)
C(8)	5 773(6)	3 185(12)	9 588(5)	C(35)	672(6)	6 302(11)	74(5)
C(17)	3 053(7)	6 047(13)	7 431(6)	O(4)	1 733(6)	–501(9)	1 017(5)
C(15)	3 392(7)	5 210(12)	6 475(6)	C(29)	3 029(7)	6 973(12)	1 474(6)
C(14)	3 521(7)	5 427(11)	7 110(6)	C(23)	3 914(8)	1 459(13)	2 980(6)
C(7)	6 331(8)	3 280(15)	10 222(5)	O(6)	3 122(5)	1 402(10)	252(5)
C(3)	5 147(6)	1 492(11)	7 912(5)	C(34)	1 494(6)	4 629(11)	–947(5)
C(18)	4 172(9)	4 036(13)	5 893(6)	C(24)	4 231(8)	2 655(14)	3 219(6)
C(10)	5 699(7)	5 604(12)	9 385(6)	C(21)	2 805(7)	1 809(12)	538(5)
C(12)	4 942(7)	6 412(10)	8 338(6)	C(30)	2 529(7)	6 671(11)	854(5)
C(5)	6 263(7)	974(14)	10 329(6)	C(36)	1 560(8)	4 045(13)	–1 544(5)
C(4)	5 718(6)	946(11)	9 688(5)	C(28)	3 343(6)	5 962(10)	1 931(5)
C(6)	6 583(8)	2 168(16)	10 582(6)	C(22)	3 370(7)	1 371(13)	2 352(5)
C(11)	5 425(8)	6 601(14)	8 984(7)	C(19)	1 904(7)	574(13)	1 017(5)

Table 4 Bond lengths (Å) and angles (°) for [ReBr(CO)$_3$(dmpbipy)]

Molecule 1				Molecule 2			
Re(1)–Br(1)	2.607(2)	O(3)–C(3)	1.139(17)	Re(2)–Br(2)	2.600(2)	C(26)–C(27)	1.479(14)
Re(1)–N(1)	2.161(7)	C(16)–C(15)	1.383(20)	Re(2)–N(6)	2.209(8)	C(32)–C(35)	1.483(18)
Re(1)–C(1)	1.887(12)	C(1)–O(1)	1.176(14)	Re(2)–C(21)	1.907(14)	C(26)–C(25)	1.398(12)
Re(1)–C(2)	1.896(9)	C(16)–C(18)	1.506(21)	O(5)–C(20)	1.173(11)	C(32)–C(33)	1.342(15)
Re(1)–N(2)	2.195(8)	C(9)–C(8)	1.473(15)	N(5)–C(22)	1.341(14)	C(27)–C(28)	1.378(14)
Re(1)–C(3)	1.896(13)	C(13)–C(12)	1.407(15)	N(7)–C(32)	1.370(12)	C(31)–C(30)	1.358(15)
N(3)–N(4)	1.382(15)	C(15)–C(14)	1.353(19)	Re(2)–N(5)	2.147(7)	C(25)–C(24)	1.364(18)
N(3)–C(14)	1.373(13)	C(9)–C(10)	1.367(16)	Re(2)–C(20)	1.889(9)	C(33)–C(34)	1.396(18)
O(2)–C(2)	1.173(11)	C(12)–C(11)	1.371(17)	Re(2)–C(19)	1.892(13)	C(21)–O(6)	1.121(19)
N(3)–C(13)	1.403(12)	C(5)–C(4)	1.383(14)	N(5)–C(26)	1.330(14)	C(36)–C(34)	1.508(18)
N(1)–C(8)	1.333(15)	C(8)–C(7)	1.381(13)	N(7)–N(8)	1.385(14)	C(22)–C(23)	1.363(15)
N(2)–C(9)	1.380(11)	C(17)–C(14)	1.490(21)	N(7)–C(31)	1.423(11)	C(24)–C(23)	1.370(19)
N(4)–C(16)	1.318(12)	C(7)–C(6)	1.361(20)	N(6)–C(31)	1.351(12)	C(30)–C(29)	1.355(15)
N(1)–C(4)	1.354(14)	C(10)–C(11)	1.314(18)	N(6)–C(27)	1.369(10)	C(28)–C(29)	1.402(16)
N(2)–C(13)	1.344(13)	C(5)–C(6)	1.378(21)	N(8)–C(34)	1.312(11)	O(4)–C(19)	1.146(16)
Br(1)–Re(1)–C(2)	91.4(4)	Re(1)–C(1)–O(1)	179.3(10)	Br(2)–Re(2)–N(6)	84.7(2)	N(7)–C(32)–C(33)	105.8(10)
C(2)–Re(1)–N(1)	174.2(4)	N(4)–C(16)–C(18)	118.7(12)	Br(2)–Re(2)–C(20)	92.1(4)	C(33)–C(32)–C(35)	133.5(9)
C(2)–Re(1)–N(2)	101.4(4)	N(4)–C(16)–C(15)	111.0(12)	N(6)–Re(2)–C(20)	102.7(4)	N(5)–C(26)–C(25)	122.4(10)
Br(1)–Re(1)–C(1)	92.6(4)	C(15)–C(16)–C(18)	130.1(10)	N(5)–Re(2)–C(21)	95.9(4)	C(25)–C(26)–C(27)	120.8(10)
N(1)–Re(1)–C(1)	97.4(4)	N(2)–C(9)–C(8)	114.5(9)	C(20)–Re(2)–C(21)	87.7(5)	N(7)–C(32)–C(35)	120.5(9)
Br(1)–Re(1)–C(3)	179.2(3)	C(8)–C(9)–C(10)	124.0(9)	N(5)–Re(2)–C(19)	96.6(4)	Re(2)–C(20)–O(5)	177.8(10)
N(1)–Re(1)–C(3)	95.5(4)	N(3)–C(13)–C(12)	118.8(10)	C(20)–Re(2)–C(19)	85.4(4)	C(26)–C(25)–C(24)	119.4(11)
C(1)–Re(1)–C(3)	87.1(5)	N(2)–C(9)–C(10)	121.5(9)	Re(2)–N(5)–C(26)	117.6(6)	C(32)–C(33)–C(34)	106.3(8)
Br(1)–Re(1)–N(1)	83.9(3)	N(3)–C(13)–N(2)	118.8(9)	C(26)–N(5)–C(22)	116.7(8)	N(6)–C(27)–C(28)	122.2(9)
Br(1)–Re(1)–N(2)	82.8(3)	N(2)–C(13)–C(12)	122.4(9)	N(8)–N(7)–C(31)	117.4(8)	N(6)–C(27)–C(26)	114.7(8)
N(1)–Re(1)–N(2)	74.7(3)	N(1)–C(8)–C(7)	122.1(11)	Br(2)–Re(2)–N(5)	84.4(3)	C(26)–C(27)–C(28)	123.1(8)
C(2)–Re(1)–C(1)	86.1(4)	N(1)–C(8)–C(9)	116.6(8)	N(5)–Re(2)–N(6)	75.0(3)	N(7)–C(31)–C(30)	118.3(8)
N(2)–Re(1)–C(1)	171.3(3)	C(9)–C(8)–C(7)	121.3(11)	N(5)–Re(2)–C(20)	175.9(4)	N(7)–C(31)–N(6)	117.1(8)
C(2)–Re(1)–C(3)	89.3(5)	N(3)–C(14)–C(17)	121.8(11)	Br(2)–Re(2)–C(21)	179.6(3)	N(6)–C(31)–C(30)	124.4(8)
N(2)–Re(1)–C(3)	97.4(4)	C(17)–C(14)–C(15)	133.0(10)	N(6)–Re(2)–C(21)	95.1(4)	Re(2)–C(21)–O(6)	173.4(10)
N(4)–N(3)–C(13)	118.1(9)	C(16)–C(15)–C(14)	107.9(9)	Br(2)–Re(2)–C(19)	91.0(5)	C(27)–C(28)–C(29)	118.7(9)
C(13)–N(3)–C(14)	128.3(10)	N(3)–C(14)–C(15)	105.2(12)	N(6)–Re(2)–C(19)	170.9(4)	C(31)–C(30)–C(29)	119.2(10)
N(4)–N(3)–C(14)	111.2(9)	C(8)–C(7)–C(6)	119.0(13)	C(21)–Re(2)–C(19)	89.3(6)	N(5)–C(22)–C(23)	124.0(11)
N(3)–N(4)–C(16)	104.6(9)	Re(1)–C(3)–O(3)	175.8(9)	Re(2)–N(5)–C(22)	125.5(7)	C(30)–C(29)–C(28)	119.2(10)
Re(1)–N(1)–C(8)	117.6(7)	C(9)–C(10)–C(11)	120.7(11)	N(8)–N(7)–C(32)	112.2(7)	N(8)–C(34)–C(36)	119.2(11)
C(8)–N(1)–C(4)	118.2(8)	C(4)–C(5)–C(6)	117.5(12)	C(32)–N(7)–C(31)	127.8(9)	N(8)–C(34)–C(33)	113.0(10)
Re(1)–N(2)–C(13)	127.2(6)	N(1)–C(4)–C(5)	122.5(11)	Re(2)–N(6)–C(31)	128.6(5)	C(33)–C(34)–C(36)	127.8(8)
Re(1)–C(2)–O(2)	177.5(9)	C(7)–C(6)–C(5)	120.5(10)	Re(2)–N(6)–C(27)	115.0(6)	C(25)–C(24)–C(23)	118.3(10)
Re(1)–N(1)–C(4)	124.1(7)	C(10)–C(11)–C(12)	121.1(12)	C(27)–N(6)–C(31)	116.1(8)	C(22)–C(23)–C(24)	119.1(12)
Re(1)–N(2)–C(9)	115.6(7)	C(13)–C(12)–C(11)	117.4(11)	N(7)–N(8)–C(34)	102.7(9)	Re(2)–C(19)–O(4)	177.9(13)
C(9)–N(2)–C(13)	116.8(8)			N(5)–C(26)–C(27)	116.8(7)		

pbipy case where these atoms are pointing outwards. The orientation of the pendant 3,5-dimethylpyrazol-1-yl ring is defined by the torsion angles N(2)–C(13)–N(3)–N(4) (molecule 1) −73.5° and N(6)–C(31)–N(7)–N(8) (molecule 2) −76.2°. These refer to the same sets of atoms as in the complex of the unsubstituted ligand and their very different magnitudes and sign indicate that the introduction of the methyl substituents at the 3 and 5 positions of the pyrazol-1-yl ring has produced a rotation of the pendant ring relative to the central pyridine ring of over 140° [142.8 (molecule 1), 151.9° (molecule 2)]. The new orientation causes the unco-ordinated nitrogen N(4) or N(8) to be *cis* to the axial carbonyl of the *fac*-ReX(CO)$_3$ moiety and the methyl–carbonyl and –bromine interactions to be minimised.

NMR spectroscopy

In Part 1 of this work[1] these pyrazolylbipyridine ligand complexes were shown to undergo 1,4-metallotropic shifts whereby the co-ordination to rhenium(I) switched between different pairs of nitrogen donors, namely the bipyridyl pair and the pyridyl/pyrazolyl pair. NMR studies at ambient and above-ambient temperatures showed that the bipyridyl-co-ordinated species were dominant in solution.

Hydrogen-1 NMR spectra of the complexes [ReX(CO)$_3$L] (L = pbipy or dmpbipy, X = Cl, Br or I; L = mpbipy, X = Br) have now been obtained in the below-ambient temperature range 30 to −100 °C using CDCl$_3$ or CD$_2$Cl$_2$ as solvents. Significant changes occurred in certain of the ^{1}H NMR signals (Table 5) which are typified by the spectra of [ReCl(CO)$_3$(pbipy)] at 303 and 178 K (Fig. 3). These changes are clearly

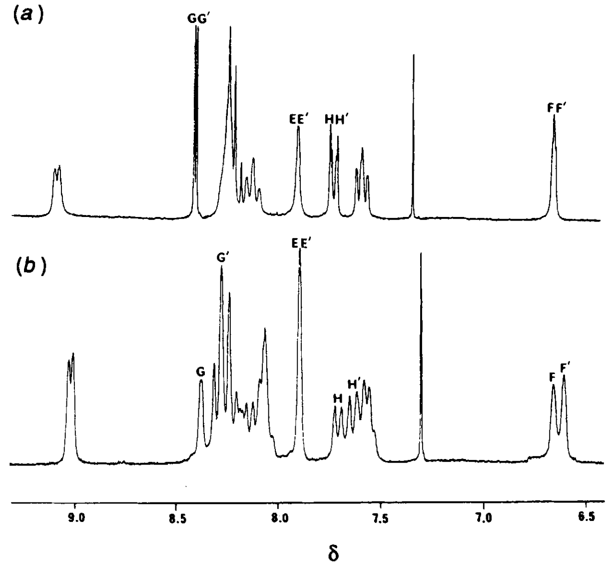

Fig. 3 Proton NMR spectra of [ReCl(CO)$_3$(pbipy)] in CD$_2$Cl$_2$ at (*a*) 303 and (*b*) 178 K. The signals most affected by the pyrazolyl-ring rotation, due to hydrogens F, G and H, are labelled

Table 5 Proton NMR chemical shift data[a] for hydrogens affected by restricted rotation in the complexes $[ReX(CO)_3L]$

Ligand, L	X	Solvent	T/K	$\delta_{E,E'}$	$\delta_{F,F'}$	$\delta_{G,G'}$	$\delta_{H,H'}$
pbipy[b]	Cl	CD_2Cl_2	303	7.91	6.66	8.42	7.74
			178	7.90	6.62	8.29	7.72
				7.90	6.67	8.38	7.65
	Br	CD_2Cl_2	273	7.91	6.66	8.28	7.68
			178	7.90	6.63	8.08	7.72
				7.90	6.67	8.24	≈7.6
	I	CD_2Cl_2	253	7.93	6.68	8.34	7.67
			178	8.03	6.63	≈8.3	7.69
				8.03	6.68	?	7.63
mpbipy[c]	Br	CD_2Cl_2	263	7.73	2.19	7.74	7.68
			178	7.74	2.20	7.99	7.86
				7.74	2.20	≈7.6	7.64
dmpbipy[d]	Cl	$(CDCl_2)_2$	263	≈2.3	6.14	≈2.3	7.47
		$CDCl_3$	213	2.33	6.20	2.38	7.51
				2.33	?	2.18	?
	Br	$(CDCl_2)_2$	263	≈2.3	6.14	≈2.3	7.45
		$CDCl_3$	218	2.33	6.19	2.38	7.49
				2.33	?	2.17	?
	I	$CDCl_3$	303	≈2.3	6.11	≈2.3	7.43
			218	2.32	6.19	2.41	7.49
				2.32	?	2.17	?

[a] Shifts relative to internal $SiMe_4$ (δ 0). [b] $R_{E,E'} = R_{F,F'} = R_{G,G'} = H$. [c] $R_{E,E'} = R_{G,G'} = H$, $R_{F,F'} = Me$. [d] $R_{E,E'} = R_{G,G'} = Me$, $R_{F,F'} = H$.

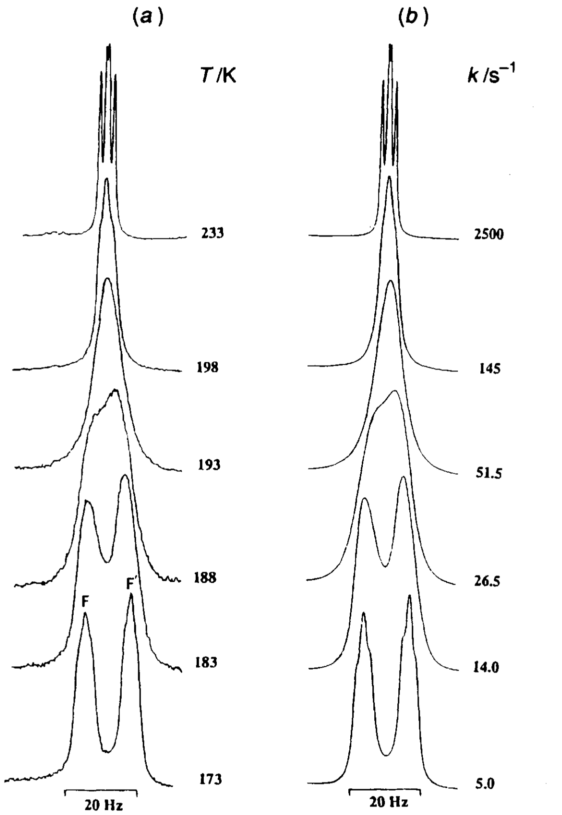

Fig. 4 Variable-temperature ^1H NMR spectra of the F, F′ hydrogens of $[ReCl(CO)_3(pbipy)]$, with theoretical bandshapes shown alongside with 'best-fit' rate constants given

associated with the arresting of the rotation of the unco-ordinated pyrazolyl ring on cooling to low temperatures. In order to follow this process the signals of the H or CH_3 groups of the pyrazol-1-yl ring, R_E, R_F and R_G, and the signal due to H_H of the pyridyl ring were carefully monitored. Signals R_F, R_G and H_H all broadened on cooling and then split into pairs of signals at the lowest temperature. These hydrogens are closest to the C–N bond about which restricted rotation of the pyrazol-1-yl ring is occurring, and therefore would be expected to be most affected by the rotation process. In the spectra of the pbipy and mpbipy complexes the band decoalescences led to near-equal-intensity pairs of signals implying that the cessation of rotation led to almost equally abundant pairs of rotameric species. In the case of the dmpbipy complexes the signal pairs were of very unequal intensities (≈98%:2%) indicating that one rotamer is strongly preferred over all others. This very different mixture of rotamers at low solution temperatures clearly reflects the significantly different orientation of the pendant 3,5-dimethylpyrazol-1-yl ring compared to the unsubstituted ring in the solid-state structures.

The changes in bandshape of the signals due to the F, F′ hydrogens were analysed in the usual way[7] taking account of the weak *ortho* spin–spin couplings and good fittings were achieved for all the pbipy and dmpbipy complexes. The case of $[ReCl(CO)_3(pbipy)]$ is shown in Fig. 4. The slightly different populations of the two rotamers causes a slight asymmetry in the band-coalescence region (188 K) and this was precisely accounted for in the bandshape analysis. The 'best-fit' rate constants are shown in Fig. 4, and these are fairly typical for all the complexes. The bandshape analyses for the dmpbipy complexes were rather more difficult to perform on account of the very unequal populations of the two rotamers. In the case of $[ReBr(CO)_3(mpbipy)]$ no distinction was observed between the Me_F and $Me_{F'}$ signals of the two rotameric species and so an estimation of the rotational barrier had to be based on the aromatic region of the spectrum. Signal-overlap problems prevented any full bandshape analysis and only an estimate of the energy barrier was possible from the coalescence of one pair of signals.

Discussion

The energy barriers associated with the restricted rotation of the unco-ordinated pyrazolyl ring in these bidentate complexes are shown in Table 6. Energies are significantly higher for the

Table 6 Energy barriers for restricted rotation of the ligand pendant heterocyclic ring in rhenium(I) complexes

Complex	X	Pendant ring	Rotamer populations	$\Delta G^{\ddagger a}$/kJ mol^{-1}	Ref.
[ReX(CO)$_3$(terpy)]	Cl	Pyridine	0.55/0.45	36.0 (41.4[b])	3
	Br	Pyridine	≈0.5/0.5	Not measurable	3
	I	Pyridine	0.5/0.5	42.8[b]	3
[ReX(CO)$_3$(pbipy)]	Cl	Pyrazole	0.505/0.495	43.4	This work
	Br	Pyrazole	0.5/0.5	43.0	This work
	I	Pyrazole	0.533/0.467	50.6	This work
[ReX(CO)$_3$(dmpbipy)]	Cl	3,5-Dimethylpyrazole	0.98/0.02	51.5	This work
	Br	3,5-Dimethylpyrazole	0.975/0.025	58.4	This work
	I	3,5-Dimethylpyrazole	0.99/0.01	*c*	This work
[ReX(CO)$_3$(mpbipy)]	Br	4-Methylpyrazole	0.5/0.5	38.5[d]	This work

[a] At 298 K. [b] At 203 K. [c] Rotamer population imbalance too great for energy-barrier measurement. [d] Estimated from measurements at the coalescence temperature (≈193 K).

dmpbipy complexes suggesting a steric influence of the methyls at the 3 and 5 positions of the pyrazolyl ring. A methyl group in the 4 position (*viz.* in the mpbipy complex) exerts no measurable steric influence. The halogen dependence of the rotation barrier is somewhat unclear but it appears that the rotation process is most restricted for iodide complexes suggesting a steric mass/size influence. In all the complexes studied pairs of static rotamers are detected at low temperatures, relative populations being near 50:50% in the case of the three pbipy complexes and the single mpbipy complex. This is analogous to the case of the terpy complexes of rhenium(I).[3] In the case of the pbipy complexes one solution rotamer is assumed to have a conformation very comparable to that associated with the crystal structure of [ReBr(CO)$_3$(pbipy)] where the orientation of the pendant ring is 36.3 (molecule 1) or 48.1° (molecule 2) and the nitrogen atom N(4) or N(8) is directed away from the axial carbonyl and is *cis* to bromine. The other rotamer is thought to correspond to the case where the ring has rotated through approximately 180° so that N(4) or N(8) is now directed towards the axial carbonyl and is *trans* to bromine. The almost equal populations of these two rotamers implies little difference in the steric interactions involving axial CO with N(4) or N(8) and C(14)–H or C(32)–H.

In contrast the very different rotamer populations of the dmpbipy complexes are attributed to the strong steric interactions of the methyl group at the 5 position of the pyrazolyl ring and the ReX(CO)$_3$ moiety. The grossly more abundant rotamer is assumed to be closely related to the solid-state structure of [ReBr(CO)$_3$(dmpbipy)] where the five-membered ring is oriented so that N(4) or N(8) is *cis* to the axial CO and the Me–CO and –Br interactions are minimised. The other rotamer, assumed to be that in which the ring has rotated through *ca.* 180°, will involve strong steric interaction between the 5-methyl group [C(17)H$_3$ or C(35)H$_3$] and the axial carbonyl group and is accordingly disfavoured.

This study shows that the different orientations of the pendant pyrazol-1-yl ring in bidentate pyrazolylbipyridine complexes of rhenium(I) which exist in the solid state lead to very different rotameric mixtures in organic solutions of these complexes. Energy barriers separating these rotameric pairs are in the range $\Delta G^{\ddagger}$ (298.15 K) 39–51 kJ mol^{-1} and increase somewhat when methyl groups occupy the 3 and 5 positions of the pendant pyrazol-1-yl ring.

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