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A remarkable temperature-dependent, accidental degeneracy of ^{31}P NMR chemical shifts in Ru(II) diphosphine/diimine complexes

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Several *cis*-RuX$_2$((*R*)-BINAP)(diimine) complexes have been prepared, and many of these exhibit an unusual temperature-dependent, accidental degeneracy of the ^{31}P shifts in their solution NMR spectra.

There is on-going research in this laboratory on Ru(II) complexes possessing one chelating, ditertiary phosphine (P–P) per Ru atom, because of their proven ability as hydrogenation catalysts,[1] especially for enantioselective catalysis when P–P is a chiral diphosphine ligand;[2] of such ligands, the C_2-symmetric BINAP (2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) and its derivatives have been employed very successfully in asymmetric catalysis.[3,4] We have also studied Ru(II) complexes with mixed P- and N-donor ligand sets, where the N-donor is either incorporated into the phosphine ligand,[5] or with separate P- and N-donor ligands,[6] and the use of Ru(II) systems with tetradentate 'P_2N_2' ligands for catalytic hydrogenation[7] and epoxidation[8] reactions has been explored recently. Of particular note, spectacular success has been achieved in the use of chiral Ru(II) complexes with phosphine (either mono- or bidentate) and diamine ligands in catalytic enantioselective hydrogenation.[4] We report here a warning concerning interpretation of the ^{31}P NMR spectra of such systems: 'apparent complications' can result from a remarkable temperature-dependent degeneracy of ^{31}P NMR chemical shifts. More specifically, some systems, where two P atoms are *trans* to different ligands (an N-donor, and a halogen), generate a singlet $^{31}P\{^1H\}$ signal resulting from an authentic, accidental degeneracy.

Complexes of formula *cis*-RuCl$_2$((*R*)-BINAP)(L$_2$), where L$_2$ = a bidentate (N–N) ligand,[†] were prepared by reaction of L$_2$ with RuCl$_2$((*R*)-BINAP)(PPh$_3$),[‡] and halide metathesis using NaX (X = Br, I) in acetone afforded the corresponding *cis*-RuX$_2$((*R*)-BINAP)(L$_2$) complexes. The structure of *cis*-RuBr$_2$((*R*)-BINAP)(bipy) (**1b**) is shown in Fig. 1.[§] The crystallographic and solution $^{31}P\{^1H\}$ NMR data (Table 1) indicate that these complexes are formed stereoselectively. For example, the pseudo-octahedral structure of **1b** has the expected[3b] λ-conformation of the (*R*)-BINAP chelate ring, and only the *R*,Λ diastereomer is seen (where Λ refers to the chirality about the Ru atom; a parallel structural refinement was carried out for both Λ and Δ isomers, but only the Λ structure refined to convergence). Further, the solution ^{31}P spectra reveal the presence of only one set of signals at any given temperature, while diastereomeric Ru(II) BINAP complexes have been differentiated by ^{31}P NMR data.[6b,9] *Cis*-**3a** is seen solely as the *R*,Δ diastereomer; whether the halide metathesis reaction occurs with retention or inversion of stereochemistry at Ru remains to be established.[10] The solution ^{31}P NMR behaviour is

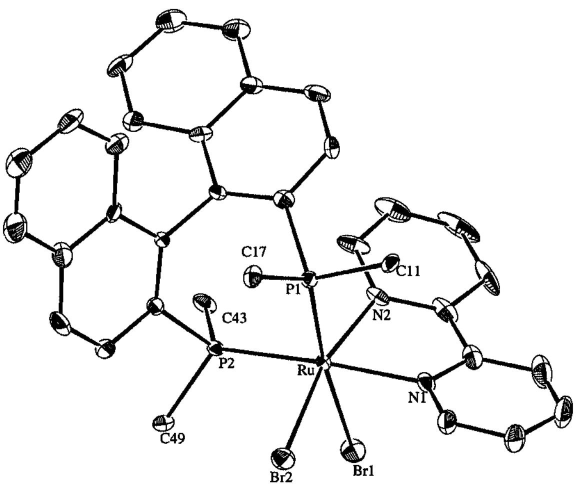

Fig. 1 ORTEP representation (50% probability ellipsoids) of *cis*-RuBr$_2$((*R*)-BINAP)(bipy) (**1b**). Solvates and H-atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ru–Br(1), 2.6175(6); Ru–Br(2), 2.5476(7); Ru–P(1), 2.305(1); Ru–P(2), 2.317(2); Ru–N(1), 2.128(4); Ru–N(2), 2.091(4); Br(1)–Ru–Br(2), 89.42(2); P(1)–Ru–P(2), 93.13(5); N(1)–Ru–N(2), 77.7(2). Only the *ipso* carbon atoms (C(11), C(17), C(43) and C(49)) of the phenyl groups are shown.

Table 1 $^{31}P\{^1H\}$ NMR spectroscopic data for *cis*-RuX$_2$((*R*)-BINAP)(L$_2$)[a]

	δ_A, δ_B [$^2J_{AB}$/Hz][b]		
Complex	C_6D_6	$CDCl_3$	CD_2Cl_2
cis-RuCl$_2$((*R*)-BINAP)(bipy) **1a**	48.0, 46.0 [32.3]	47.1, 46.6 [33.5][c]	47.2[d]
cis-RuBr$_2$((*R*)-BINAP)(bipy) **1b**	47.8, 45.2 [32.1]	47.3, 46.7 [33.3][e]	47.2, 46.9 [33.7][f]
cis-RuI$_2$((*R*)-BINAP)(bipy) **1c**	49.4, 42.5 [30.0]	48.8, 44.2 [30.6]	48.4, 44.6 [31.7]
cis-RuCl$_2$((*R*)-BINAP)(dmbipy) **2**	47.5, 47.2 [33.4][g]	48.3, 47.4 [34.6]	48.0, 47.5 [34.4]
cis-RuCl$_2$((*R*)-BINAP)(phen) **3a**	48.4, 46.2 [34.0]	47.2[h]	47.9, 47.5 [34.4][i]
cis-RuBr$_2$((*R*)-BINAP)(phen) **3b**	48.7, 45.7 [32.8]	48.0, 47.0 [33.1][j]	47.5, 46.9 [34.0][k]
cis-RuI$_2$((*R*)-BINAP)(phen) **3c**	50.8, 42.6 [29.7]	49.6, 44.6 [31.3]	49.3, 45.2 [31.5]
cis-RuCl$_2$((*R*)-BINAP)(batho) **4**	47.8, 45.5 [33.4]	47.6, 46.9 [33.6]	47.4, 47.1 [33.7][l]
cis-RuCl$_2$((*R*)-BINAP)(bpa) **5**	50.7, 47.1 [33.3]	50.0, 47.6 [33.5]	49.5, 48.0 [33.6]

[a] Satisfactory elemental analyses were obtained for all the complexes listed.[10] [b] At room temperature (~20 °C) except where noted (121 MHz spectrometer frequency). [c] At 50 °C: δ 47.2 (s). [d] At −30 °C: δ_A = 47.8, δ_B = 47.4 [33.8]; at 35 °C: δ_A = 47.4, δ_B = 47.0 [34.5]. [e] At −60 °C: δ 47.3 (s). [f] At 10 °C: δ 47.2 (s); at −20 °C: δ_A = 47.6, δ_B = 47.2 [32.9]. [g] At 25 °C: δ 47.3 (s); at 40 °C: δ_A = 47.4, δ_B = 47.0 [33.6]. [h] At −30 °C: δ_A = 47.8, δ_B = 47.2 [34.4]; at 60 °C: δ_A = 47.2, δ_B = 46.9 [33.9]. [i] At 0 °C: δ 47.9 (s); at −90 °C: δ_A = 48.4, δ_B = 48.1 [34.9]. [j] At −40 °C: δ 47.7 (s). [k] At −10 °C: δ 47.6 (s); at −20 °C: δ_A = 47.6, δ_B = 47.2 [32.9]. [l] At 25 °C: δ 47.2 (s).

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remarkable in that the expected AB pattern is sometimes ‘lost’ (Table 1). Thus, **3a** in $CDCl_3$ shows a singlet (δ 47.2) in its room temperature spectrum, while in CD_2Cl_2 an AB pattern (δ_A = 47.9, δ_B = 47.5, $^2J_{AB}$ = 34.4 Hz) is present; **1a** demonstrates the opposite behaviour (an AB pattern in the $CDCl_3$ spectrum and a singlet in CD_2Cl_2).

Variable temperature (VT) NMR studies, conducted on all the complexes, are exemplified by the data shown in Fig. 2. From 0 to 10 °C, the spectrum of **1b** consists of a sharp singlet, while an AB pattern is observed either side of this range with increasing separation of the signals; there is clearly no dynamic exchange process between, for example, two species giving a time-averaged singlet. A temperature-dependent, accidental degeneracy of the two signals of the 4-line AB pattern gives rise to the singlet. At a specific solvent and temperature combination, an A_2 pattern is observed, the ^{31}P nuclei having become isochronous. This degeneracy occurs in at least one solvent studied (usually chlorinated) for most of the *cis*-RuX_2((*R*)-BINAP)(L_2) complexes, while *cis*-$RuCl_2$((*R*)-BINAP)(dmbipy) (**2**) is the only complex exhibiting degeneracy in C_6D_6 and not in $CDCl_3$ or CD_2Cl_2. The dibromo complexes **1b** and **3b** exhibit degeneracy at lower temperatures than the corresponding dichloro analogues (**1a** and **3a**); the diiodo complexes (**1c** and **3c**) show no degeneracy from −90 to 60 °C. Changing from the planar bipy- or phen-based ligand systems (**1**–**4**) to that with bis(*o*-pyridyl)amine (**5**) sufficiently separates the two ^{31}P shifts that degeneracy is not seen (Table 1). The related *cis*-$RuCl_2$(DPPB)(L_2) complexes (DPPB = 1,4-bis(diphenylphosphino)butane) possess well separated ($\Delta\delta$ > 10) signals in their ^{31}P NMR spectra.[6c]

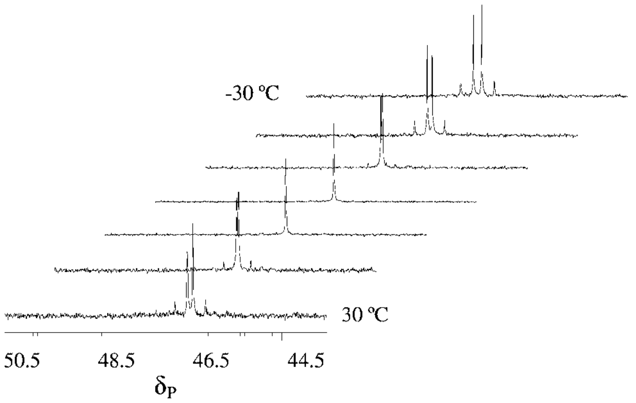

Fig. 2 VT $^{31}P\{^1H\}$ NMR spectra (CD_2Cl_2, 121 MHz) of *cis*-$RuBr_2$((*R*)-BINAP)(bipy) (**1b**) from 30 to −30 °C. Spectra are plotted in 10 °C increments.

Such accidental degeneracy is likely involved in some ‘anomalies’ in earlier work from this laboratory. Within the L(DPPB)Ru(μ-Cl)$_3$*Ru*Cl(DPPB) complexes (L = nitrile), a $^{31}P\{^1H\}$ singlet, rather than the expected AB (or AX) pattern, is seen for the two P atoms at *Ru* at 20 °C in CD_2Cl_2 (*i.e.* a singlet and 2 doublets are observed), while the expected 4 doublets are seen in C_6D_6 or $CDCl_3$;[6b] at −40 °C in CD_2Cl_2 the 2 sets of AB patterns are seen.[11] When L is Me_2S, the AB pattern is seen at 20 °C in C_6D_6, but not in $CDCl_3$, while the reverse holds true when L is tetrahydrothiophene, although VT NMR experiments were not performed.[12]

The temperature-dependence of ^{31}P NMR shifts is well documented, and indeed has been used for measuring sample temperature in VT work; *e.g.* the δ_P values for PPh_3 and O=PPh_3 change linearly with temperature (~1.3 Hz °C).[13] Further, the temperature-dependence of the δ_P values for the dimetallic, mixed-halide ClPd(μ-DPPM)$_2$PdI species (DPPM = bis(diphenylphosphino)methane) formed *in situ* varies with solvent, and the A_2B_2 pattern observed in $CDCl_3$ at −20 °C ‘collapses’ to a singlet at 35 °C, and reemerges above 45 °C,[14] behaviour similar to that of our Ru complexes.

To our knowledge, the *cis*-RuX_2((*R*)-BINAP)(L_2) complexes are the first isolated complexes to exhibit temperature-dependent degeneracy of ^{31}P NMR shifts. These data, particularly the observance of the degeneracy at room temperature in common NMR solvents, indicate that caution should be taken in the analysis of ^{31}P NMR data, especially for the widely studied chiral P–P systems, where such spectra remain a major characterization technique. The ‘impossible’ observation of a singlet NMR signal *must* be interrogated further by variation of temperature *and* variation of solvent.

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Notes and references

† Abbreviations used are: bipy (2,2′-bipyridine), dmbipy (4,4′-dimethyl-2,2′-bipyridine), phen (1,10-phenanthroline), batho (4,7-diphenyl-1,10-phenanthroline, or bathophenanthroline) and bpa (bis(*o*-pyridyl)-amine).

‡ A representative synthesis is as follows: $RuCl_2$((*R*)-BINAP)(PPh_3)[1b] (0.19 g, 0.18 mmol) and bipy (0.37 g, 0.24 mmol) were dissolved in 7 mL of C_6H_6 and the solution was refluxed for 3 h. The orange product (**1a**, L_2 = bipy), precipitated by the addition of 30 mL hexanes, was washed with hexanes and dried *in vacuo*. Yield: 0.11 g (65%). Anal. Calc. for $C_{54}H_{40}N_2Cl_2P_2Ru$: C, 68.21; H, 4.24; N, 2.95. Found: C, 68.24; H, 4.23; N, 3.01%.

§ *Crystal data* for **1b**: $C_{54}H_{40}N_2Br_2P_2Ru\cdot3C_6D_6$, M = 1292.09, monoclinic, space group $P2_1$, a = 13.3564(7), b = 14.2879(7), c = 15.4367(9) Å, β = 98.448(4)°, V = 2913.9(2) Å^3, Z = 2, D_c = 1.473 g cm^{-3}, μ = 17.45 cm^{-1}, T = −100 °C, 25153 reflections measured, 6590 unique (R_{int} = 0.089), R (R_w) = 0.079 (0.092) on all data. X-ray crystal data are also available for **3a** and **5**.

CCDC reference number 164469. See http://www.rsc.org/suppdata/cc/b1/b103473c/ for crystallographic data in CIF or other electronic format.

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