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1,2-Metallotropic shifts in tricarbonylrhenium(I) complexes of pyridazine (pydz): a dynamic NMR investigation of the effects of *cis*-chelating ligands

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Abstract

Complexes of general formula *fac*-[Re(CO)₃(L–L)(pydz)][BF₄] (L–L = neutral bidentate chelate ligand; pydz = pyridazine) were prepared in high yield from *fac*-[ReBr(CO)₃(L–L)]. The pyridazine ligand coordinates to the metal moiety in a monodentate fashion, and undergoes a facile intramolecular 1,2-Re–N shift. The kinetics of the 1,2-metallotropic shift were measured by either one-dimensional NMR bandshape analysis or two-dimensional exchange spectroscopy. The free energies of activation, ΔG^{\neq} (298 K), were found to be dependent on the nature of the chelate ligand, and were in the range 77–87 kJ mol⁻¹. The origins of the chelate ligand effects are discussed.

Keywords: Rhenium complexes; Chelate ligand complexes; Fluxional pyridazine complexes; Dynamic NMR

1. Introduction

The stereochemical non-rigidity associated with monodentate diazine-transition metal complexes is well established [1-8]. In these complexes, the diazine ligand undergoes a facile 1,2-metallotropic shift between the two contiguous N donor atoms, via a mechanism which is believed to involve a 20-electron N,N' σ -bonded transition state [4,5,7,9]. The authors embarked recently on a systematic approach to the study of the factors which affect the energetics of transition metal-diazine rearrangements; we report here the results of our studies on the effect of cis-chelate ligands in complexes of general formula fac-[Re(CO)₃(L–L)(pydz)][BF₄] (L-L = neutral bidentate chelate ligand; pydz = pyridazine).These complexes, which are readily prepared from fac- $[\text{ReBr}(\text{CO})_3(\text{L-L})]$ by the action of AgBF₄ in the presence of pyridazine, are kinetically inert and thermally stable. Thus they provide an excellent substrate for the quantitative investigation of the effects of the cis-chelating ligands on the fluxional rearrangement.

2. Experimental

2.1. Materials

Bromopentacarbonylrhenium(I) was prepared from dirheniumdecacarbonyl as previously described [10,11]. The proligands and pyridazine were purchased from standard sources (Aldrich or Lancaster Syntheses Ltd.) and were used as supplied.

2.2. Synthesis of the complexes

Manipulations were performed using standard Schlenk techniques [12], under an atmosphere of dry, oxygen-free nitrogen. Solvents were dried [13] and degassed prior to use. The precursor complexes, [ReBr(CO)₃(L–L)] (L–L= 2,2'-bipyridine (bipy), 2,2'-bipyrimidine (bpym), 1,10-phenanthroline (phen), N,N,N',N'-tetramethylethylenediamine (tmen) or bis(diphenylphosphino)ethane (dppe)), were prepared in an analogous fashion to that reported for the 2,2':6',2"-terpyridine complex, [ReBr(CO)₃(terpy)] [14], as illustrated by the synthesis of [ReBr(CO)₃(bipy)].

2.2.1. [(Bipyridyl)bromotricarbonylrhenium(I)]

Bromopentacarbonylrhenium(I) (1.0 g, 2.46 mmol) was dissolved in 30 cm³ of 50:50 (vol./vol.) benzene/80–100 light petroleum. 2,2'-Bipyridine (0.48 g, 2.56 mmol) was

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^{0020-1693/97/\$17.00 © 1997} Elsevier Science S.A. All rights reserved $\it PII\,S\,0\,0\,20-1\,6\,93\,(\,9\,6\,)\,0\,5\,3\,3\,9-X$

added to the stirred solution and the reaction mixture was then refluxed for ~ 2.5 h. Concentration of the benzene at reduced pressure yielded a yellow solid, which was isolated by filtration and dried in vacuo. No further purification was necessary. Yield: 1.18 g (94%).

The five complexes, fac-[Re(CO)₃(L–L)(pydz)][BF₄] (L–L = bipy, bpym, phen, tmen or dppe), were all prepared similarly. The preparation of [Re(CO)₃(bipy)(pydz)]-[BF₄] is detailed below to illustrate the synthetic procedure.

2.2.2. [(Bipyridyl)(pyridazine)tricabonylrhenium(I)]-[tetrafluoroborate]

(Bipyridyl)bromotricarbonylrhenium(I) (1.0 g, 1.97 mmol) and AgBF₄ (0.50 g, 2.56 mmol) were refluxed for ~ 1 h in 30 cm³ of tetrahydrofuran (THF). The reaction mixture was then filtered (to remove AgBr), and added to a stirred THF solution of pyridazine (0.25 g, 3.12 mmol in 5 cm³). The THF solution was refluxed for ~ 1 h, then the volatile components were removed in vacuo. The resultant orange oil was crystallised from ethylethyl ketone–diethyl ether to yield 0.70 g (60%) of solid [Re(CO)₃(bipy)-(pydz)][BF₄].

2.3. Physical methods

IR spectra were recorded as pressed CsI discs on a Nicolet Magna 550 FT-IR spectrometer, operating in the region $4000-200 \text{ cm}^{-1}$. Fast atom bombardment (FAB) mass spectra were obtained on a VG AutoSpec instrument, using Cs⁺ bombardment at 25 kV energy, on the complexes dissolved in a matrix of 3-nitrobenzyl alcohol. Elemental analyses were performed by Butterworth Laboratories Ltd., Teddington, Middlesex.

¹H NMR spectra were recorded as d₆-DMSO solutions on a Bruker AM250 Fourier Transform spectrometer, operating at 250.13 MHz. Chemical shifts are quoted in ppm, relative to tetramethylsilane as an internal standard. Probe temperatures were controlled by a standard B-VT 1000 unit. Temperatures were periodically checked against a (Comark) digital thermometer, and are considered accurate to within ± 1 °C. Two-dimensional exchange (EXSY) spectra were obtained using the Bruker automation program NOESYPH [15], which generates the pulse sequence $D1-90^{\circ}-D0-90^{\circ}$ - $D0-90^{\circ}$ -free induction decay. The relaxation delay, D1, was 2.0 s and the evolution time, D0, was initially set at 3 μ s. The mixing time, D9, was varied according to the temperature of the experiment and complex under investigation; typically D9 was in the range 0.05-1.0 s. The spectra were recorded with 512 words of data in f_1 and f_2 , and transformed with 1024 words. The total experiment times were typically ~ 2.5 h. Peak intensities were measured by volume integration of the resulting two-dimensional spectra. Five sets of integrations were performed on each of the spectra; mean values were then used to calculate the exchange rate constants using the D2DNMR program [16]. Five or six EXSY experiments were performed at different temperatures on each of the complexes, $[\text{Re}(\text{CO})_3(\text{L}-\text{L})(\text{pydz})][\text{BF}_4]$ (L–L = bipy, bpym, phen or dppe). Rate data for the complex $[\text{Re}(\text{CO})_3(\text{tmen})(\text{pydz})][\text{BF}_4]$ were obtained by the simulation of standard one-dimensional variable temperature spectra. 13 spectra were recorded in the temperature range 297–368 K, and the band shape changes were analysed using the authors' version of the program DNMR3 [17]. Computer simulated spectra were visually fitted with those experimentally obtained, until a 'best-fit' was achieved. Rate data for the five complexes, $[\text{Re}(\text{CO})_3(\text{L}-\text{L})(\text{pydz})][\text{BF}_4]$ (L–L = bipy, bpym, phen, tmen or dppe), were used to calculate the activation parameters from least-squares fits of the Eyring and Arrhenius plots. The errors quoted are those defined by Binsch and Kessler [18].

3. Results

The five complexes, $[Re(CO)_3(L-L)(pydz)][BF_4](L-L)$ = bipy, bpym, phen, tmen or dppe), were isolated as crystalline orange solids as described (vide supra). The complexes (except L-L=bpym) are air-stable for periods of several weeks under ambient conditions; however, they do decompose slowly on prolonged exposure to air. The IR spectra displayed three bands in the carbonyl stretching region, and up to nine bands each due to the Re-C stretching and deformation modes. These data are consistent with a facoctahedral coordination geometry for the ReBr(CO)₃ metal moiety [19]. Fast atom bombardment (FAB) mass spectrometry was performed on the five complexes; in all cases (except L-L=dppe), molecular ions were observed for the species $[Re(CO)_3(L-L)(pydz)]^+$. The complex [Re- $(CO)_3(dppe)(pydz)$ [BF₄] exhibited a molecular ion attributable to $[M - BF_4 - CH_2]^+$. In all cases, the observed isotope distribution patterns were consistent with those calculated for the formulated species. The elemental analyses obtained for the complexes $[Re(CO)_3(L-L)(pydz)][BF_4]$ (L-L=bipy, phen, tmen or dppe) were consistent with the formation of analytically pure samples. The somewhat low C and N analyses for the 2,2'-bipyrimidine complex, $[Re(CO)_3(bpym)(pydz)][BF_4]$, probably arise because of some partial decomposition of the complex (vide supra). Analytical data for the five complexes, $[Re(CO)_3(L-L)-$ (pydz) [BF₄] (L–L = bipy, bpym, phen, tmen or dppe), are reported in Table 1.

3.1. NMR studies

3.1.1. Complexes $[Re(CO)_3(L-L)(pydz)][BF_4](L-L=bipy, bpym or phen)$

The ambient temperature (303 K) ¹H NMR spectra of the complexes [Re(CO)₃(L–L)(pydz)][BF₄] (L–L=bipy, bpym or phen) in d₆-DMSO solution displayed well resolved signals. The spectra comprised two overlapping sub-spectra in the region ca. δ 7.5–9.5, due to (i) the proligands (bipy, bpym or phen) and (ii) the hydrogens of the pyridazine ring.

Table 1			
Synthetic and analytical data for the complexes	$[Re(CO)_{2}(L-L)(pvdz)]^{+}BE$	$^{-}$ (I $-$ I $_{-}$ = bipy bpym	phen_tmen_or_dppe)

Complex (chelate ligand)	Yield ^a	ν (C–O) ^b (cm ⁻¹)	ν (Re–C) ^b (cm ⁻¹)	Anal. Found (Calc.)	m^+/z^{c}
(enclute ligand)	(70)	(cm)	(em)	(70)	
bipy	60	1920.8 ^b	385.0, 408.4, 420.0,	C, 34.54 (34.41)	507
		2030.3	484.0, 521.8, 539.7,	H, 2.01 (2.04)	
			628.9, 642.6	N, 9.46 (9.44)	
bpym	12	1925.4	386.1, 398.6, 413.1,	C, 25.34 (30.26)	509
		1959.7	420.4, 479.6, 522.1,	H, 1.71 (1.69)	
		2040.0	539.8, 627.0, 644.7	N, 11.67 (14.12)	
phen	75	1916.6 ^b	384.9, 414.1, 473.3,	C, 36.62 (36.97)	531
		2029.9	482.4, 522.0, 540.3,	H, 1.76 (1.96)	
			546.1, 625.8, 645.9	N, 9.12 (9.08)	
tmen	70	1904	395.0, 417.8, 455.5,	C, 27.49 (28.22)	467
		1935	481.3, 520.0, 534.9,	H, 3.27 (3.64)	
		2032	641.1, 652.0	N, 9.84 (10.13)	
dppe	70	1934	370.6, 383.2, 435.2,	C, 46.81 (47.44)	735 ^d
		1967	495.4, 515.5, 604.9,	H, 3.15 (3.38)	
		2039	618.4	N, 3.21 (3.55)	

^a Yield quoted relative to $[ReX(CO)_3(L-L)]$.

^b IR spectra recorded as CsI discs; not all bands observed, b = broad.

^c FAB mass spectral data; ions observed correspond to $[M - BF_4]^+$, except for dppe ^d.

^d Observed ion corresponds to the species $[M - BF_4 - CH_2]^+$.

The signals due to the proligands were assigned on the basis of their scalar coupling networks (determined from a series of selective homonuclear decoupling experiments) and by comparison with the spectra for the analogous Pt^{IV} complexes, $[PtMe_3(L-L)(pydz)][BF_4](L-L=bipy, bpym or phen)$ [8]. The sub-spectra due to the pyridazine ring displayed three resonances in a 1:1:2 intensity ratio, indicative of the ligand acting as a non-exchanging, monodentate ligand [4,5]. The 3- and 6-position hydrogen atoms, H_A and H_B (Fig. 1), were assigned on the basis that H_A would be expected to resonate to higher frequency as a result of its close proximity to the metal-coordinated N atom [5,7]. The 4- and 5-position hydrogens, H_C and H_D , have almost iden-



Fig. 1. The complexes $[Re(CO)_3(L-L)(pydz)][BF_4](L-L=bipy, bpym or phen)$ showing the H atom labelling in the ligands.

tical chemical shifts and could not be distinguished unambiguously. The spectrum of $[Re(CO)_3(phen)(pydz)][BF_4]$ is shown in Fig. 2. ¹H NMR data are reported in Table 2.

On warming solutions of the complexes above ~ 380 K, the resonances due to H_A and H_B displayed dynamic line broadening, indicating the onset of the expected 1,2-Re–N fluxional shift (Fig. 3) at a measurable rate. Magnetisation transfers also occur between H_C and H_D as a result of the 1,2-Re–N shift; however, the close proximity of these signals (vide supra) renders them insensitive to the rearrangement. On warming the solutions further, considerable thermal decomposition of the complexes was evident, and it was not possible to acquire a reliable set of standard one-dimensional variable temperature spectra. Kinetic data were therefore sought by two-dimensional exchange spectroscopy (2D-EXSY). Accordingly, five EXSY experiments were performed on each of the complexes, $[Re(CO)_3(L-L)-(pydz)][BF_4]$ (L–L= bipy, bpym or phen), and accurate



Fig. 2. 250 MHz ¹H NMR spectrum of $[Re(CO)_3(phen)(pydz)][BF_4]$ in $(CD_3)_2SO$ solution at 303 K. Labelling refers to Fig. 1.

Table 3

= bipy, bpym, phen or dppe)

Table 2
^1H NMR data a for the complexes [Re(CO)_3(L–L)(pydz)] $^+\text{BF}_4$ $^-$ (L–L
= bipy, bpym, phen, tmen or dppe)

Temperature $\delta(pydz-H)^{b,c}$ δ (chelate) ^{b,c} Complex (chelate ligand) (K) 303 A, 9.51 (4.9) E, 9.34 (5.5) bipy B, 8.96 (4.8) F. 7.9 C, 7.9 G, 8.44 (7.7, 8.2) H, 8.75 (8.2) D, 7.9 303 A, 9.54 (4.4) E. 9.3 bpym B, 8.82 (4.5) F, 7.98 G, 9.3 C. 7.9 D, 7.9 A, 9.24 (4.2) ^d 303 E, 9.62 (5.2) phen B, 8.31 (4.2)^d F, 8.20 (8.3, 5.2) C, 7.7 G, 9.00 (8.3) D. 7.7 H, 8.29 A, 9.47 (4.4) 297 Me, 2.66 tmen B, 9.65 (4.3) Me, 3.25 C, 8.0 CH₂, 2.93 D, 8.1 CH₂, 3.47 303 A, 9.97 (5.6) CH₂, 5.6 dppe B, 8.05 (4.5) CH₂, 6.1 C, 7.83 (8.1 $J_{\rm CD})$ D, 7.50 (8.1 $J_{\rm CD}$)

^{a 1}H NMR spectra recorded in (CD₃)₂SO solution; chemical shifts quoted relative to SiMe₄ as an internal standard.

 $^{b 3}J(HH)/Hz$ in parentheses; not all scalar couplings resolved.

^c Labelling refers to Figs. 1 and 4.

^d Also ${}^{4}J(HH) = 2.9$ Hz, ${}^{5}J(HH) = 1.3$ Hz.



Fig. 3. Effects of the 1,2-metallotropic shift in $[Re(CO)_3(L-L)-(pydz)][BF_4]$ complexes on the pydz hydrogen environments.

rate data extracted from the magnetisation transfers between signals due to H_A and H_B (Table 3). The activation parameters calculated from the rate data are reported in Table 4.

3.1.2. Complex $[Re(CO)_3(dppe)(pydz)][BF_4]$

The ¹H NMR spectrum of $[\text{Re}(\text{CO})_3(\text{dpp})(\text{pydz})]$ - $[\text{BF}_4]$ in d₆-DMSO 303 K was well resolved, and comprised two regions: (i) the proligand (dppe) methylene region (ca. δ 5.6–6.1) and (ii) the aromatic region (ca. δ 7.4–10.0). The proligand methylene region displayed two complex secondorder multiplets in a 1:1 intensity ratio. The lower frequency resonance was tentatively assigned to the hydrogen atoms *cis* with respect to pyridazine (Fig. 4), as these might be expected to be slightly shielded (relative to the hydrogen environments *trans* to pyridazine) by the aromatic ring current. The spectrum in the aromatic region comprised a complex overlapping signal due to the hydrogen atoms of the

Complex (chelate ligand)	Temperature (K)	Rate ^a (s ⁻¹)
bipy	338	0.52
	343	0.85
	348	1.15
	353	2.03
	358	3.47
bpym	338	0.31
	343	0.44
	348	0.99
	353	2.15
	358	3.02
	363	3.47
phen	338	0.35
•	343	0.46
	348	0.97
	358	2.97
	363	3.35
	368	4.23
dppe	353	0.51
	358	1.13
	368	2.37
	378	4.84
	383	5.01

2D EXSY data for the complexes $[Re(CO)_3(L-L)(pydz)]^+BF_4^-$ (L-L

^a First order rate constants for the 1,2-metal–nitrogen shift process; uncertainties are ca. $\pm 10\%$.

proligand phenyl rings, and three signals in a 1:1:2 intensity ratio due to the four different hydrogen environments of the non-exchanging pyridazine ring. The pyridazine hydrogen signals were assigned to H_A , H_B and $H_{C/D}$, respectively (vide supra). ¹H NMR data are reported in Table 2.

On warming the d₆-DMSO solution of $[Re(CO)_3(dpp)-(pydz)][BF_4]$ above ~ 358 K, the signals due to the 3- and 6-position hydrogen atoms of the pyridazine ring, H_A and H_B, exhibited reversible dynamic line broadening, as a result of the onset of the 1,2-Re–N shift at a measurable rate on the NMR chemical shift time scale. At higher temperatures, the complex started to decompose, thus frustrating attempts to acquire a reliable set of variable temperature spectra. Kinetic data were therefore sought by 2D EXSY NMR. Five EXSY experiments were performed in the temperature range 353–383 K and accurate rate data obtained for the metallotropic shift (Table 3). The activation parameters calculated from the rate data are reported in Table 4.

3.1.3. Complex $[Re(CO)_3(tmen)(pydz)][BF_4]$

The ¹H NMR spectrum of $[\text{Re}(\text{CO})_3(\text{tmen})(\text{pydz})]$ -[BF₄] in d₆-DMSO solution at 297 K exhibited well resolved signals. The spectrum consisted of regions due to (i) the proligand (tmen) hydrogen atoms (ca. δ 2.6–3.5), and (ii) the pyridazine ring hydrogen atoms (ca. δ 8.0–9.7). The pyridazine region of the spectrum displayed three signals, characteristic of the ligand acting as a non-exchanging monodentate ligand (vide supra). These signals were tentatively

6	n
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Complex (chelate ligand)	$E_{\rm a}$ (kJ mol ⁻¹)	$\frac{\log_{10}}{(A\ (s^{-1}))}$	ΔH^{\neq} (kJ mol ⁻¹)	$\frac{\Delta S^{\neq}}{(\mathrm{J}\mathrm{mol}^{-1}\mathrm{K}^{-1})}$	ΔG^{\neq} (kJ mol ⁻¹)
bipy	93.9 (5.8)	14.2 (0.9)	91.0 (5.8)	17.6 (16.6)	85.8 (0.8)
bpym	109 ^b	16.4 (1.7)	106 ^b	58.4 (31.9)	88.8 (1.7)
phen	93.4 (8.2)	14.0 (1.2)	90.5 (8.3)	12.8 (23.4)	86.7 (1.3)
tmen	113.8 (2.2)	19.1 (0.3)	110.0 (2.2)	111.8 (6.4)	77.7 (0.3)
dppe	84.6 (9.9)	12.3 (1.4)	81.6 (9.9)	-19.0 (27.0)	87.2 (1.9)

Table 4 Eyring and Arrhenius activation parameters ^a for the complexes $[Re(CO)_3(L-L)(pydz)]^+BF_4^-(L-L=bipy, bpym, phen, tmen or dppe)$

^a Errors given in parentheses; ΔG^{\neq} values quoted at 298.15 K.

^b Error uncertain.





Fig. 4. The complexes $[Re(CO)_3(L-L)(pydz)][BF_4]$ (L-L=dppe or tmen) showing the hydrogen labelling.

assigned to H_B , H_A and $H_{C/D}$ (Fig. 4), respectively, by comparison with the ¹H NMR spectrum of the corresponding Pt^{IV} complex, $[PtMe_3(tmen)(pydz)][BF_4]$ [8]. It should be noted that, in contrast to the Re^I complexes described here, the assignment of H_A and H_B in the Pt^{IV} complexes is unambiguous because H_A displays measurable ³J scalar coupling to ¹⁹⁵Pt (I = 1/2, 33% abundance). Thus it is not possible to establish if the anomalously high frequency shift of H_B observed in [PtMe₃(tmen)(pydz)][BF₄] also occurs in the complex $[Re(CO)_3(tmen)(pydz)][BF_4]$; the assignments of H_A and H_B may therefore be reversed. This uncertainty in the assignment of H_A and H_B does not affect the measurement of the exchange kinetics (vide infra). The proligand (tmen) region comprised two complex second-order multiplets due to the methylene hydrogen atoms, and two singlets due to the N-methyls. In each case, the lower frequency signal was tentatively assigned to the cis-hydrogen environments, Fig. 4. ¹H NMR data are reported in Table 2.

On raising the NMR probe temperature, magnetisation transfers resulting from the expected 1,2-Re–N metallotropic shift lead to broadening of the pyridazine ring hydrogen signals. These line shape changes can be followed by standard one-dimensional bandshape analysis according to the dynamic spin problem ABCD \Rightarrow BADC [4], and the temperature dependent spectra were simulated on this basis. The signals due to H_C and H_D are insensitive to the exchange process owing to their close proximity; therefore, only the line shape changes associated with H_A and H_B were subject to analysis (Fig. 5). Some thermal decomposition of the complex [Re(CO)₃(tmen)(pydz)][BF₄] is evident from its ¹H NMR spectra, but this did not adversely affect the band



Fig. 5. Experimental and computer simulated variable temperature ¹H NMR spectra of $[\text{Re}(\text{CO})_3(\text{tmen})(\text{pydz})][\text{BF}_4]$. The 'best-fit' rate constants are given with the computer simulated spectra. 'Best-fit' rate constants for other temperatures are as follows: $k(s^{-1}) = 1.0$ (313 K), 2.8 (318 K), 12 (328 K), 32 (338 K), 325 (358 K), 550 (363 K) and 900 (368 K).

shape fittings and twelve reliable rate constants were obtained, six of which are shown in Fig. 5. The Eyring and Arrhenius activation parameters calculated for the 1,2-metallotropic shift are reported in Table 4.

4. Discussion

The activation parameters obtained for the 1,2-Re–N fluxional shift in the complexes $[Re(CO)_3(L-L)(pydz)][BF_4]$ (L-L=bipy, bpym, phen, tmen or dppe) are reported in Table 4. Examination of the magnitudes of the free energies of activation, ΔG^{\neq} (298 K), reveals a dependence on the chelate ligand, the trend being bpym>dppe>phen> bipy \gg tmen. The same trend was observed in the analogous platinum(IV) complexes, $[PtMe_3(L-L)(pydz)][BF_4]$ (L-L=bipy, bpym, phen or tmen) [8], and may be rationalised in terms of a decrease in the M–N(pydz) interaction concomitant with an increase in the metal-chelate ligand interaction. Thus the observed trend in ΔG^{\neq} (298 K) would be expected to be inversely related to the relative trans influence of the chelate ligands; i.e. the magnitude of ΔG^{\neq} (298 K) would be expected to decrease as the trans influence of the chelate ligand increases. It is not possible to corroborate this hypothesis in the present complexes, since the relative trans influences of the chelate ligands cannot be measured. In contrast, measurements of the ${}^{2}J(Pt-CH_{3})$ scalar couplings in the analogous Pt^{IV} complexes enables a qualitative estimate of the relative trans influences of the chelate ligands to be obtained [20,21]. It was found [8] that the ${}^{2}J(\text{PtCH}_{3})$ scalar couplings were in the order bpym>phen>bipy> tmen, indicating that the trans influence increases from 2,2'bipyrimidine to N, N, N', N'-tetramethylethylenediamine. The observed trend in ΔG^{\neq} (298 K) is also in accord with the pK_a values for the free proligands, pK_a bpym < dppe < phen < bipy < tmen. However, it should be noted that pK_a values are not always a reliable indicator of the relative coordinating abilities of ligands [22].

Since the chelate ligands are cis to the fluxional Re-N(pydz) bond, no strong dependence was anticipated, and changes in ΔG^{\neq} (298 K) are generally small ($\Delta (\Delta G^{\neq}) \sim 3$ kJ mol⁻¹ for L–L=bipy, bpym, phen or dppe). However, the substantial decrease in the observed free energy of activation for the 1,2-metallotropic shift in the tmen complex, $[Re(CO)_3(pydz)][BF_4]$, clearly cannot be rationalised solely in terms of strong Re-N(tmen) interactions. It seems likely that the considerable decrease in ΔG^{\neq} (298 K) stems primarily from a destabilisation of the Re-N(pydz) bond, as a result of steric interactions between the tmen N-methyl groups and the fluxional pyridazine ring. The sizable entropy of activation, ΔS^{\neq} , for the complex [Re(CO)₃(tmen)-(pydz)][BF₄] helps to support this hypothesis. An anomalously low magnitude for the free energy of activation was also obtained for the analogous Pt^{IV} complex, [PtMe₃-(tmen)(pydz)][BF₄] [8]. A similar lowering of the free energy of activation might be expected for the bis(diphenylphosphino)ethane complex, $[Re(CO)_3(dppe)(pydz)]$ - $[BF_4]$, as a result of steric interactions between the dppe phenyl rings and the pyridazine ligand. However, the planar phenyl rings are able to orient in such a way as to minimise such interactions; thus, in contrast to the tmen complex, the observed magnitude of ΔG^{\neq} (298 K) is not dominated by the steric requirements of the proligand.

With the exception of the tmen complex (vide supra), the free energies of activation are similar to those obtained for the bis(pyridazine) complexes [ReX(CO)₃(pydz)₂] (X=Cl, Br or I) [5], i.e. in the range ~ 85–87 kJ mol⁻¹. It might be expected that a small increase in ΔG^{\neq} (298 K) would be observed on going from a neutral species to a cationic metal moiety. However, the effect of the positive charge on the metal centre can be largely offset by a decrease in the $d\pi$ -p π backbonding to the carbonyls. In accord with previously noted trends, the present Re^I complexes have a higher free energy of activation than the analogous Pt^{IV} complexes [PtMe₃(L–L)(pydz)][BF₄] (L–L=bipy, bpym, phen or tmen) [8]. This presumably reflects the relative strengths of the fluxional M–N(pydz) bonds.

5. Conclusions

The energetics of the Re–N 1,2-metallotropic shift in the complexes [Re(CO)₃(L–L)(pydz)][BF₄] (L–L=bipy, bpym, phen or dppe) are sensitive to the nature of the chelate ligand. This dependence may be rationalised in terms of changes in the metal–chelate ligand bonding interactions, and is in accord with the trends noted previously for the analogous platinum(IV) complexes. The substantial decrease in the relative magnitude of ΔG^{\neq} (298 K) when the is employed as the chelate ligand is presumed to result from large steric interactions between the N-methyl groups and the fluxional pyridazine ring.

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