Stereochemically non-rigid transition metal complexes of 2,6-bis[(1-phenylimino)ethyl]pyridine (BIP)
Part 1. Dynamic NMR studies of $[M(C_6F_5)_2(BIP)]$ ($M = Pt^{II}$ or Pt^{II})

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Abstract

The complexes $[M(C_6F_5)_2(BIP)]$ ($M = Pd^{II}$ or Pt^{II}, BIP = 2,6-bis[(1-phenylimino)ethyl]pyridine) have been synthesised and characterised as involving BIP as a bidentate chelate ligand. In solution they undergo 1,4 metallotropic shifts of the $M(C_6F_5)_2$ moiety, E,Z isomerisation of the pendant imine bond, and restricted C–C rotation of the pendant portion of the BIP ligand. ^1H and ^{19}F dynamic NMR studies yielded activation energies for these three types of fluxion. $\Delta G^{\neq}$ (298 K) values for the three processes were 89.6, 86.6 and 47.4 kJ mol^{-1} respectively for the Pt^{II} complex. Values for the Pd^{II} complex were significantly lower in magnitude, namely 71.6, 70.4 and 41.8 kJ mol^{-1} respectively.

1. Introduction

Complexes such as $[Pd(C_6F_5)_2(diox)_2]$ [1,2], $[M(C_6F_5)_2(THF)_2]$ (M = Pd [3] or Pt [4]), *trans*-$[Pd(C_6F_5)_2(tht)_2]$ [5] (tht = tetrahydrothiophene) and *cis*-$[M(C_6F_5)_2(PhCN)_2]$ (M = Pd [6,7] or Pt [8]) have been shown to be excellent precursors for the synthesis of pentafluorophenyl derivatives of these metals. These complexes undergo facile exchange reactions with bidentate chelate ligands to form complexes containing *cis*-$M(C_6F_5)_2$ moieties. The ligand 2,2':6',2''-terpyridine (terpy) reacts with *trans*-$[M(C_6F_5)_2(diox)_2]$ (M = Pd or Pt, diox = 1,4-dioxane) to form the square planar complexes *cis*-$[M(C_6F_5)_2(terpy)]$ (terpy = 2,2':6',2''-terpyridine) in which the terpyridine acts in a bidentate chelate mode [9]. In solution these complexes are fluxional with terpyridine oscillating between equivalent bidentate modes by a postulated 'tick–tock' twist mechanism. Rates for this fluxional motion and for restricted rotation of the pendant ligand ring were measured by dynamic NMR techniques [9].

In order to investigate the generality of the 1,4 metallotropic shift in metal complexes containing poten-

tially terdentate pyridine-based ligands, it was decided to extend the study to ligands involving N donor atoms in non-heterocyclic systems in the 2 and 6 positions of pyridine. These ligands are of interest in homogeneous catalytic reactions, especially those mediated by organopalladium or -platinum compounds [10]. In this context the compound 2,6-bis[(1-phenylimino)ethyl]-pyridine (BIP) (Fig. 1), a potentially terdentate ligand involving the donor set N_3 which forms five-membered chelate rings, is well suited for the study. In fact, the coordinating ability of BIP is comparable [11,12] with that of terpyridine, the most widely studied of this class of ligand [13]. BIP usually bonds to a metal as a terdentate ligand [12], but a few complexes have been reported [14,15] in which it exhibits a bidentate chelate mode of bonding. In this work we explore the properties of BIP acting as a bidentate chelate ligand towards the moiety $M(C_6F_5)_2$ (M = Pd or Pt).

2. Results

The complexes *cis*-$[M(C_6F_5)_2(BIP)]$ (M = Pd or Pt) have been prepared by substitution reactions using *trans*-$[Pd(C_6F_5)_2(diox)_2]$ and *cis*-$[Pt(C_6F_5)_2(Et_2S)_2]$ re-

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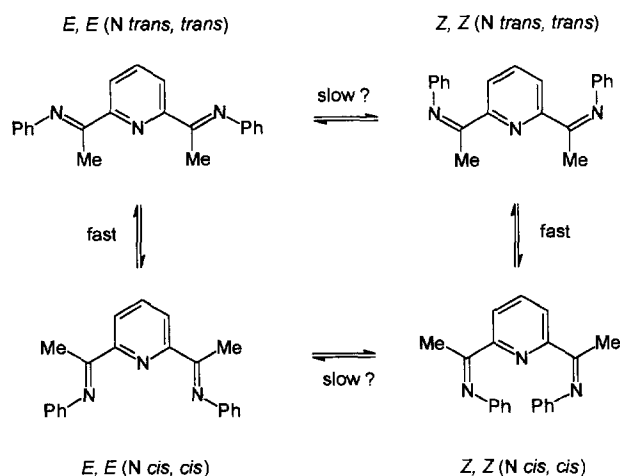E, E (N trans, trans)   Z, Z (N trans, trans)

Fig. 1. Some conformers of 2,6-bis-[(1-phenylimino)ethyl]pyridine (BIP).

spectively. They were obtained in moderate yields as air-stable solids. Infrared spectra of these complexes were an aid to their stereochemistry. Strong absorptions for Pd(II) at 808 and 788 cm^{-1} and for Pt(II) at 819 and 801 cm^{-1} were indicative of mutually cis-C_6F_5 groups bonding to the metal. The bands at ~ 800 cm^{-1} are of particular use for structural diagnosis, and have been assigned to an 'X-sensitive' mode [16,17] that has mainly $\nu(M–C)$ character [18,19]. For square planar complexes of $M(C_6F_5)_2$, the presence of two bands in this region is characteristic of a non-linear C–M–C skeleton, i.e. cis-$M(C_6F_5)_2$, while only one band is found for those derivatives with a linear C–M–C skeleton, i.e. $trans$-$M(C_6F_5)_2$. Further characterisation was achieved by elemental analyses (Table 1) and ^{1}H/^{19}F NMR spectra (Table 2).

2.1. ^{1}H NMR studies

The free ligand spectrum at 30 °C consists of five sets of aromatic signals and a methyl signal. These are consistent with a ligand having C_{2v} symmetry with a mirror plane bisecting the pyridyl ring through the heterocyclic N atom and the 4 position of the ring.

Signal assignments are given in Table 2. This spectrum is compatible with any of the four structures shown in Fig. 1, or any average of these forms. The preferred conformational forms of this ligand were identified by NOE difference experiments. Irradiation of the methyl signal gave a strong enhancement of the $ortho$ phenyl hydrogen signal and a very weak enhancement of the 3,5-pyridyl hydrogens. Irradiation of the $ortho$ and $meta$ phenyl hydrogens gave a methyl signal enhancement in addition to a $para$ phenyl enhancement, and irradiation of the 3,5-pyridyl hydrogens gave a strong 4-pyridyl hydrogen enhancement only. These results strongly indicate that the preferred conformers of BIP have E-substitution at each imine double bond, and the favoured structure is that where the three N atoms of the ligand adopt a $trans/trans$ relationship. Exchange between these structures will be rapid on the NMR timescale at ambient temperatures as a result of C–C rotation of the imine substituents. It is thought probable that a low percentage of Z,Z conformers (Fig. 1) is also present, in view of the coordination properties of this ligand (see later). Exchange between the E,E and Z,Z forms, probably by N inversion, is likely to be slow on the NMR timescale, but no separate NMR signals were detected, presumably due to overlaps with the major set. On coordination, 11 signals of BIP are detected, indicating that the ligand is acting in a bidentate, five-membered chelate mode of bonding to the metal. Careful analysis of the spectra involving proton-decoupling experiments and an NOE difference study on cis-[Pt(C_6F_5)$_2$(BIP)] established an unambiguous assignment of all protons (Table 2). The assignment of the signal arising from Me_F was based on the fact that irradiation of Me_F caused a strong NOE with the pyridyl H_G (Fig. 2(a)), whereas irradiation of Me_J (Fig. 2(b)) caused only a slight NOE with pyridyl H_I. This is interpreted as indicating that Me_F is part of the coordinated imine moiety, whereas Me_J is associated with the pendant part of the ligand where its average distance from H_I is large due to rotation about the bond linking the imine moiety to the pyridyl ring. Surprisingly, the Me_F and Me_J groups in the Pd(II) complex are almost isochronous.

Table 1
Analytical data for the complexes cis-$M(C_6F_5)_2$(BIP)] (M = Pd or Pt)

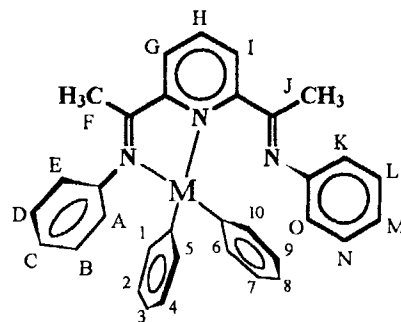| Complex	M.p. (°C)	Yield [a] (%)	$\nu(M–C)$ [b] (cm^{-1})	Analysis [c] (%)			Appearance
				C	H	N	
[Pd(C_6F_5)$_2$(BIP)]	218–221 (decomp.)	39.0	808s	(52.57)	(2.54)	(5.57)	Cream powder
			788s	52.23	2.39	4.85	
[Pt(C_6F_5)$_2$(BIP)]	219–222	42.1	819s	(47.04)	(2.27)	(4.99)	Bright yellow powder
			801s	47.55	2.35	4.75	

[a] Yield quoted relative to metal-containing reactant.
[b] Recorded as CsI discs; s = strong.
[c] Calculated values in parentheses.

Table 2

¹H NMR data [a] for complexes cis-[M(C₆F₅)₂(BIP)] (M = Pd or Pt) in CD_2Cl_2 at 30°C (300.13 MHz)

Compound	δ_A J_{AB} J_{AC}	δ_B J_{BC} J_{BD}	δ_C J_{CD} J_{CE}	δ_D J_{DC} J_{DB}	δ_E J_{ED} J_{EC}	δ_F	δ_G J_{GH} J_{GI}	δ_H J_{HG} —	δ_I J_{IH} J_{IG}	δ_J	δ_K J_{KL} J_{KM}	δ_L J_{LM} J_{LN}	δ_M J_{MN} J_{MO}	δ_N J_{NM} J_{NL}	δ_O J_{ON} J_{OM}
BIP	dm 6.86 8.2 —	tm 7.40 8.2 —	tt 7.14 8.2 1.1	tm 7.40 8.2 —	dm 6.86 8.2 —	s 2.41 — —	d 8.37 7.8 —	t 7.90 7.8 —	d 8.37 7.8 —	s 2.41 — —	dm 6.86 8.2 —	tm 7.40 8.2 —	tt 7.14 8.2 1.1	tm 7.40 8.2 —	dm 6.86 8.2 1.1
[Pd(C₆F₅)₂(BIP)]	d 6.78 7.6 —	t 7.22 7.7 —	t 7.12 6.8 —	t 7.22 7.7 —	d 6.78 7.7 —	s 2.40 — —	dd 8.07 8.1 2.6	t 8.28 8.1 —	dd 8.07 8.1 2.6	s 2.39 — —	d 6.50 7.7 —	t 7.30 7.6 —	t 7.12 6.8 —	t 7.30 7.6 —	d 6.50 7.7 —
Δδ	−0.08	−0.18	−0.02	−0.18	−0.08	−0.01	−0.30	0.38	−0.30	−0.02	−0.36	−0.10	−0.02	−0.10	−0.36
[Pt(C₆F₅)₂(BIP)]	dm 6.82 7.4 —	t 7.25 7.8 —	tt 7.16 7.4 1.3	t 7.25 7.8 —	dm 6.82 7.4 —	s 2.24 — —	t 8.07 7.9 —	t 8.37 7.9 —	td 8.07 7.9 —	s 2.45 — —	d 6.55 7.4 —	tm 7.31 7.4 —	tt 7.12 7.4 1.1	tm 7.31 7.4 —	d 6.55 7.4 —
Δδ	−0.04	−0.15	0.02	−0.15	−0.04	−0.17	−0.30	0.47	−0.30	0.04	−0.31	−0.09	−0.02	−0.09	−0.31

[a] Chemical shifts (δ) relative to TMS, $\delta = 0$; $\Delta\delta = \delta_{complex} - \delta_{ligand}$; s = singlet, d = doublet, t = triplet, m = multiplet. Scalar couplings in hertz.

The ^1H spectra at 30 °C show signals for the isochronous pairs of *ortho* and *meta* protons of each phenyl ring. This is consistent with the fast rotation of these rings on the chemical shift timescale. It is notable that all the *ortho* and *meta* protons show low frequency shifts relative to the free ligand. This is attributed to the anisotropic shielding effect of the C_6F_5 rings.

The very small magnitude of the coordination shifts $\Delta \delta$ of the *ortho* signals H_A, H_E shows that these hydrogens are far less affected than the *meta* hydrogens H_B, H_D. The shielding effects on the other phenyl ring show the converse. This is consistent with a structure whereby the anisotropic magnetic field of the C_6F_5 ring *trans* to the pyridyl unit affects the *meta* signals H_B, H_D of the adjacent phenyl ring, while the other C_6F_5 group mostly affects the *ortho* signals due to the flexibility of the pendant part of the BIP ligand. Both *para* hydrogens are near the periphery of this shielding effect. Hydrogens H_G and H_I, which are surprisingly isochronous in both complexes, show a substantial low frequency shift as expected due to inductive effects in the *meta* position of the pyridyl ring when coordination occurs. The difference in magnitude of the high fre-

quency coordination shifts of signal H_H for the complexes is probably the only 'pure' measure of the difference in electrophilicity of these metal moieties. The Pt(II) complex shows a relative increase in the deshielding of the anisotropic field; hence H_H resonates at an appreciably higher frequency.

In the spectra of both metal complexes there is evidence of another species being present, as shown in Fig. 2 for the Pt(II) complex. In the aromatic region of the spectrum it was not possible to assign the signals due to the minor species because many of them overlap with those of the major species. In the methyl region of the ^1H spectra of both Pd(II) and Pt(II) complexes, pairs of minor signals appear at frequencies lower than the signals of the major species. Since the elemental analyses of these complexes were reliable, the major and minor species were thought to be due to structures involving isomerisation of the pendant imine bond of the BIP ligand, namely *E,E* and *E,Z* isomers, Fig. 3. The major species will be the *E,E* structure in view of the preferred conformation of the free ligand, and from the evidence of the NOE difference experiment on the Pt(II) complex where irradiation of $Me_{F/J}$ causes signal
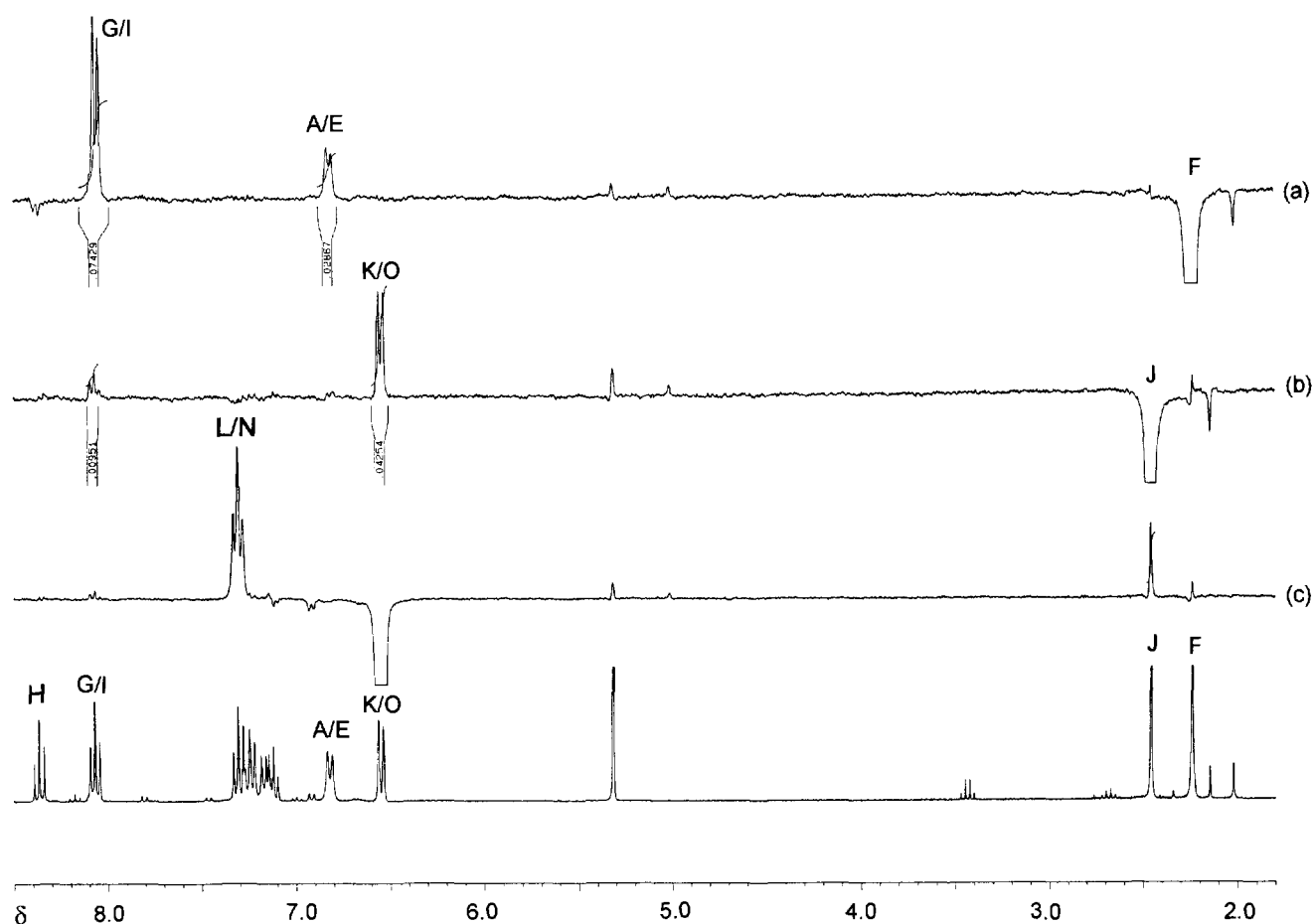

Fig. 2. 400 MHz ^1H NMR NOE difference experiments of *cis*-[Pt(C_6F_5)$_2$(BIP)] in CD_2Cl_2 showing the effects of irradiation at (a) Me_F, (b) Me_J and $H_{O/K}$.

enhancements of the *ortho* ring hydrogens $H_{A/E}$ and $H_{K/O}$ (Fig. 2). In the Pd(II) complex the minor, presumed E,Z isomer, was present in 9% abundance and, in the Pt(II) case, in 7.3% abundance (Table 3).

2.2. ^{19}F NMR spectra

At room temperature the ^{19}F NMR spectra of the E,E isomers exhibit three signals for each C_6F_5 ring (Table 4). This pattern is typical of an AA′MM′X system in which the two *ortho* fluorine nuclei and the two *meta* fluorine nuclei are isochronous. On cooling to $-80\,^{\circ}C$ the signals due to the *ortho* and *meta* signals become split and the spectra show features typical of a first-order five-spin system, i.e. an AFMRX system, which corresponds to a molecule in which ring rotation has been arrested. The assignment of the signals of the two C_6F_5 rings is only tentative, being based on the tentative assignments made for the analogous terpy complexes [9].

The ^{19}F spectrum of the Pt(II) complex shows satellites due to coupling between ^{195}Pt and the *ortho* ring ^{19}F nuclei. Usually such couplings are useful in distinguishing between *cis* and *trans* forms of $Pt(C_6F_5)_2$ when bound to N donors. For instance, in the case of *cis*- and *trans*-[Pt(C$_6$F$_5$)$_2$(py)$_2$] (py = pyridine) it was found that whilst the *cis* compound had a coupling $J_{PtF} = 473\,Hz$, the magnitude of the coupling in the *trans* compound was $J_{PtF} = 275\,Hz$. *Trans* structures, in general, have smaller couplings. Other *cis*-bound imine ligands show couplings of similar magnitude, namely *cis*-[Pt(C$_6$F$_5$)$_2$(phen)] (phen = 1,10-phenanthroline) where the J_{PtF} coupling is 460 Hz and *cis*-[Pt(C$_6$F$_5$)$_2$(en)] (en = ethane-1,2-diamine) where it is 473 Hz. In the present case these couplings were 435 Hz for both rings. As they have the same magnitude they cannot be used to differentiate between the two C_6F_5 rings. As signals for the E,Z isomers were mostly overlapping with the major E,E species, it was not possible to assign their ^{19}F NMR spectra.

2.3. Dynamic NMR studies

The solution dynamics of the complexes *cis*-[M(C$_6$F$_5$)$_2$(BIP)] (M = Pd or Pt) were investigated by variable temperature studies. Three processes were investigated: (i) 1,4 metallotropic shifts; (ii) geometrical
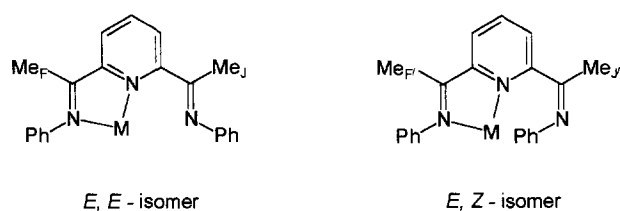
E, E - isomer   E, Z - isomer

Fig. 3. The E,E and E,Z isomers of M^{II} (BIP) complexes.

Table 3
^1H NMR data [a] of methyl region for complexes *cis*-[M(C$_6$F$_5$)$_2$(BIP)] (M = Pd or Pt) in CD$_2$Cl$_2$ at 30 °C (300.13 MHz)

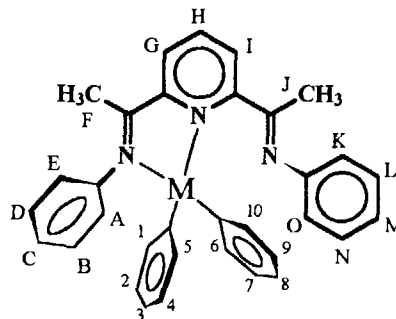| Compound	E,E isomer		E,Z isomer	
	F	J	F′	J′
	Abundance (%)		Abundance (%)	
[Pd(C$_6$F$_5$)$_2$(BIP)]	2.40	2.39	2.19	2.09
	91.0		9.0	
[Pt(C$_6$F$_5$)$_2$(BIP)]	2.24	2.45	2.02	2.15
	92.7		7.3	

[a] Chemical shifts (δ) relative to TMS, $\delta = 0$.

isomerisation at the imine bond; and (iii) restricted rotation process(es).

Processes (i) and (ii) proved to be interdependent for quantitative dynamic NMR study and will be discussed next. Both complexes gave similar ^1H NMR spectra at room temperature, indicative of bidentate imine ligand species. On heating the NMR solutions all spectral lines broadened, except for signal H_H, with pairs of lines eventually coalescing and then sharpening. This is the result of fluxional processes involving the metallotropic shifts of the pair of M–N bonds and E,Z isomerisation in the pendant imine bond (Scheme 1). In the Pt(II) complex rates for both types of fluxional process were deduced by complete bandshape analysis of the exchanging pairs of methyl groups. The fittings are shown alongside experimental spectra in Fig. 4. This was possible by using the exchange scheme (Scheme 2). Here the labelling refers to Fig. 3. F and J are the methyl signals for the major species, the E,E isomer, and F′ and J′ are the methyl signals for the minor species, the postulated E,Z isomer. The only pure metallotropic shift involves the J ⇌ F exchange measured by the rate constant k_1. The rate constants k_3, k_5 and k_6 all measure rates for the composite exchange involving simultaneous metallotropic shift and E,Z isomerisation. These are unlikely events and therefore their rates were assumed to be approximately zero. Both rate constants k_2 and k_4 measure the same process, pure $E,E \rightleftharpoons E,Z$ isomerisation, and therefore their magnitudes should be identical at all temperatures. This simplifies the dynamic problem to the measurement of only two magnitudes of rate constant, namely k_1 and $k_2 = k_4$, at all temperatures. These magnitudes were obtained by fitting the signals F,F′ and J,J′ (Fig. 4).

Since the two methyl signals for the major species were almost isochronous in the case of the Pd(II) complex, rates for the metallotropic shift and isomerisation of this complex were calculated in a different way. The metallotropic shift was monitored by its exchange effect on the *ortho* hydrogens of the phenyl rings, namely H_A/H_E and $H_{O/K}$. Three-bond spin–spin couplings to the adjacent *meta* hydrogens were allowed for in the bandshape analysis (Fig. 5). By fitting these signals,

Table 4

^{19}F NMR data [a] for complexes cis-$[M(C_6F_5)_2(BIP)]$ (M = Pd or Pt) in CD_2Cl_2 (282.36 MHz)

Compound	T (°C)	δ_1 / J_{12} / J_{13}	δ_2 / J_{23} / J_{24}	δ_3 / J_{34} / J_{35}	δ_4 / J_{43} / J_{42}	δ_5 / J_{54} / J_{53}	δ_6 / J_{67} / J_{68}	δ_7 / J_{78} / J_{79}	δ_8 / J_{87} / J_{86}	δ_9 / J_{98} / J_{97}	δ_{10} / $J_{10,9}$ / $J_{10,8}$
[Pd(C$_6$F$_5$)$_2$(BIP)]	−80	d [b] 47.41 / 33.5 / —	m −1.57 / — / —	t 2.50 / 21.2 / —	m 1.57 / — / —	d [b] 46.98 / 33.5 / —	d [b] 44.17 / 32.4 / —	m −1.32 / — / —	t 1.00 / 21.2 / —	m −0.05 / — / —	d [b] 45.7 / 32.4 / —
[Pd(C$_6$F$_5$)$_2$(BIP)]	30	dd [b] 47.51 / 22.7 / 5.8	m −2.35 / — / —	t 1.51 / 20.0 / —	t [b] −2.35 / 21.1 / —	dd [b] 47.51 / 22.7 / 5.8	d [b] 45.01 / 29.1 / —	t [b] −1.66 / 21.3 / —	t −0.06 / 20.0 / —	t [b] −1.66 / 21.3 / —	d [b] 45.01 / 29.1 / —
[Pt(C$_6$F$_5$)$_2$(BIP)]	−80	t [b] 43.61 / 30.8 / —	m −2.59 / — / —	t 1.22 / 20.8 / —	m −2.59 / — / —	t [b] 43.61 / 30.8 / —	d [b] 40.68 / 30.4 / —	m −2.59 / — / —	m −0.25 / 20.7 / —	m −0.93 / — / —	d [b] 44.00 / 30.6 / —
[Pt(C$_6$F$_5$)$_2$(BIP)]	30	d [b] 44.25 / 30.2 / J_{Pt-F} 435	m −3.53 / — / —	t [b] 0.35 / 19.9 / —	m −3.53 / — / —	d [b] 44.25 / 30.2 / J_{Pt-F} 435	s [c] 42.41 / — / J_{Pt-F} 435	m −2.60 / — / —	t [b] −1.32 / 19.8 / —	m −2.60 / — / —	s [c] 42.41 / — / J_{Pt-F} 435

[a] Chemical shifts (δ) relative to C_6F_6 ($\delta = 0$); s = singlet, d = doublet, t = triplet, m = multiplet. Scalar couplings $|J_{ij}|$ in hertz.

[b] Signal with further multiplicity.

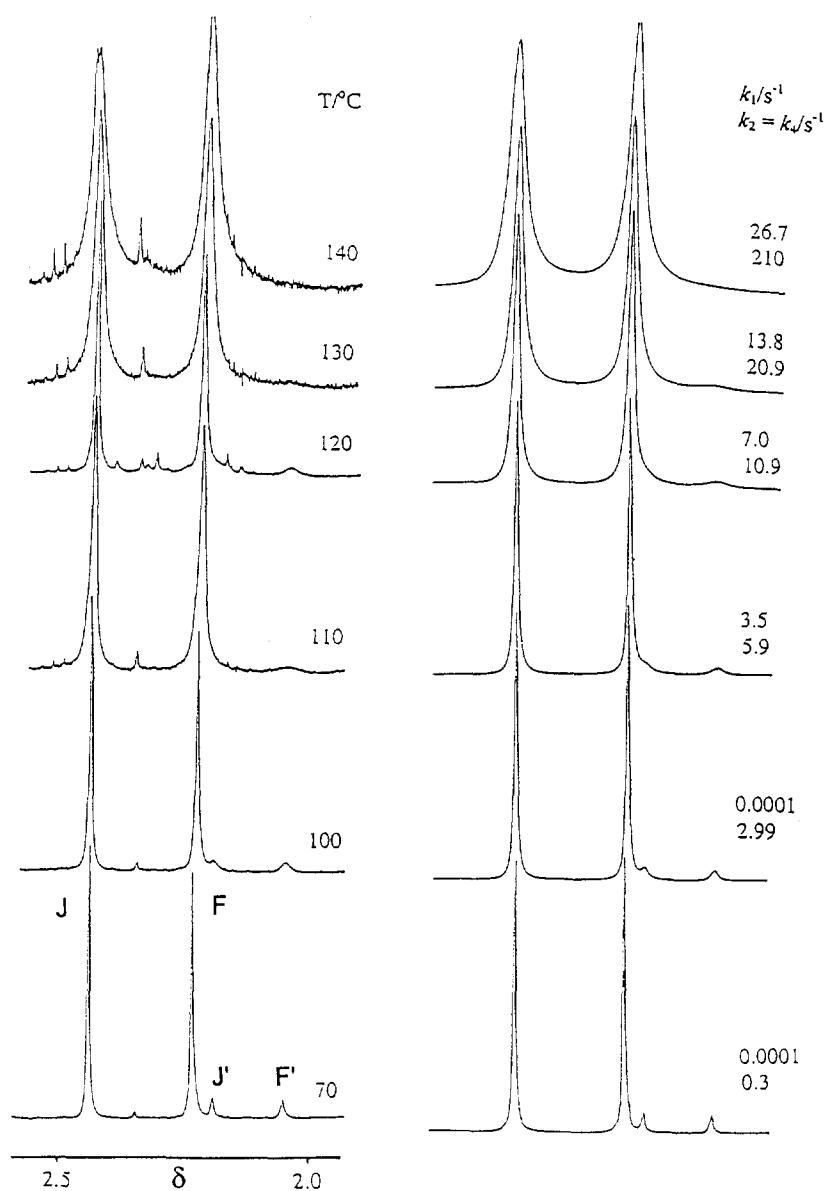[c] Not well resolved at this temperature.
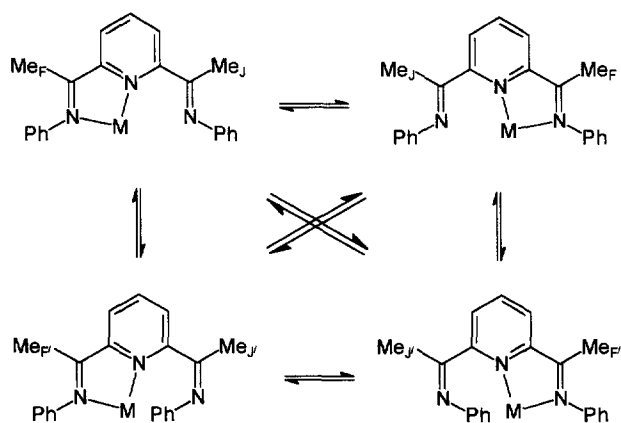
Scheme 1.
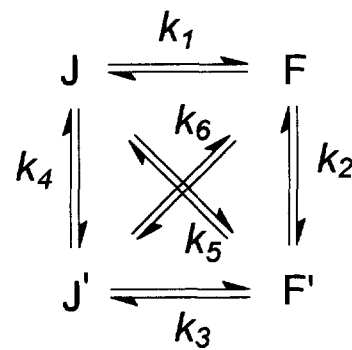
Scheme 2.

Fig. 4. 300 MHz ^{1}H NMR spectra (methyl region) of cis-[Pt(C$_6$F$_5$)$_2$(BIP)] in (CDCl$_2$)$_2$ showing the effects of 1,4 metallotropic shifts and imine E,Z ⇌ E,E isomerisation processes. Theoretical spectra with 'best-fit' rate constants for both processes are shown alongside.

reliable rate constants were derived, Fig. 5. An approximate rate constant for the geometrical isomerisation of the pendant imine bond in the Pd(II) complex was deduced from the coalescence of the signal pairs F/F' and J/J'. This coalescence occurred at 90 °C.

In order to be able to propose a mechanism for the fluxional process the behaviour of the ancillary C_6F_5 ligands was studied, utilising their ^{19}F nuclei as probes. A variable temperature ^{19}F study in the same temperature range (30–120 °C) as the ^{1}H study showed exchange between the magnetically inequivalent pairs of *ortho* and *meta* fluorine nuclei as well as exchange between the *para* fluorine nuclei (Fig. 6). Exchange between the two C_6F_5 rings, occurring in conjunction with the ligand exchange process, provides evidence that the mechanism can be considered to be via a five-coordinate intermediate in which all three nitrogen donor atoms are associated with the metal (Scheme 3).

There are two possible mechanisms for the E,Z isomerisation, namely via a C=N bond rotation or via a nitrogen inversion. In the present studies it is not possible to definitely exclude either mechanism. However,

on the basis of previous studies [20], it would appear that N inversion is the more likely mechanism for geometrical isomerisation in these complexes.

The free ligand BIP has been shown to exist preferentially as an E,E isomer. By reaction with an appropriate metal centre it forms two metal complexes; $[M(C_6F_5)_2(E,E\text{-BIP})]$ as the major complex and $[M(C_6F_5)_2(E,Z\text{-BIP})]$ as the minor species. Both complexes involve the ligand acting as a bidentate chelate to the metal. The complexes are distinguished by the pendant part of the ligand, showing an E or Z configuration of the imine bond. In order to be involved in the metal commutation motion, the pendant imine part of the ligand has to be the E isomer. The E,Z isomer is prevented from undergoing M–N commutation because the electron pair of the heterodonor points away from the metal at all times, even when allowance is made for rotation about the C–C bond of the pendant part of the BIP ligand. Therefore in order for the E,Z isomer to undergo a metallotropic shift, isomerisation of the pendant part must first occur. It was found that the isomerisation and the metallotropic shift occur with activation
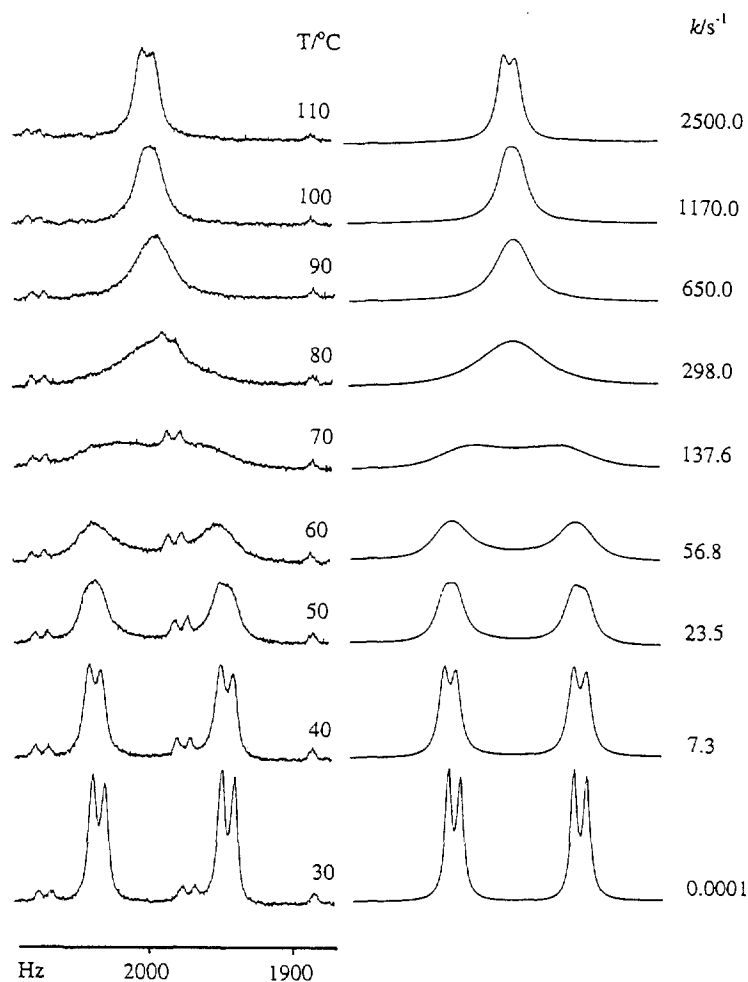

Fig. 5. 300 MHz ^{1}H NMR spectra (aromatic region) of *cis*-[Pd(C_6F_5)$_2$(BIP)] in $(CDCl_2)_2$ in the temperature range 30–110 °C showing the effects of metallotropic shifts on the *ortho* ring hydrogens.
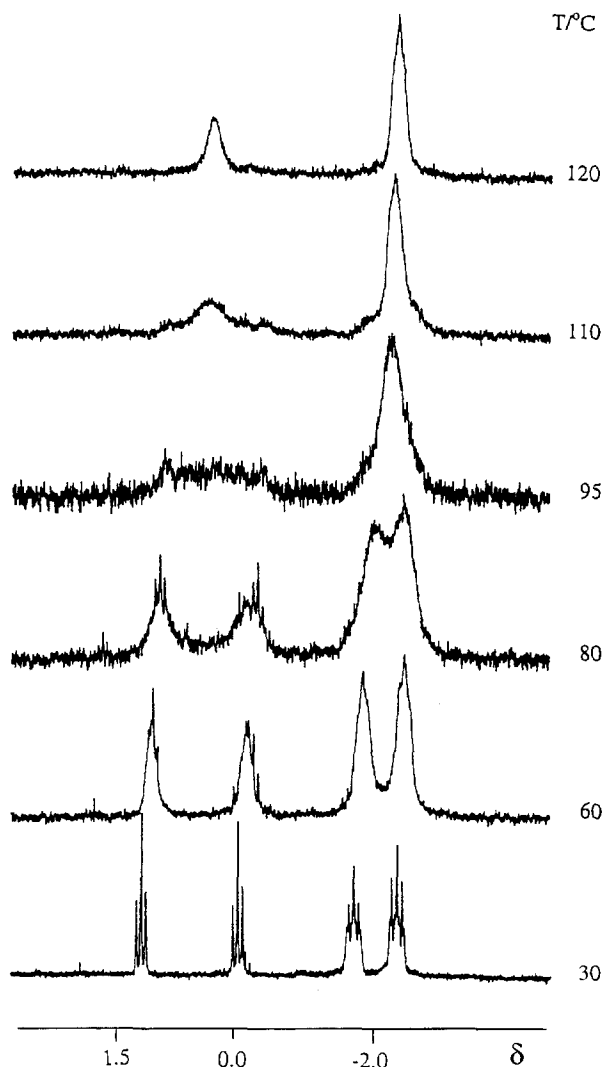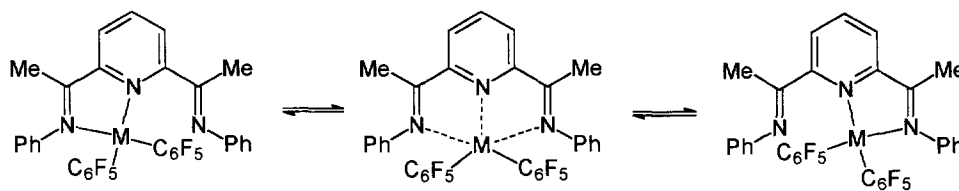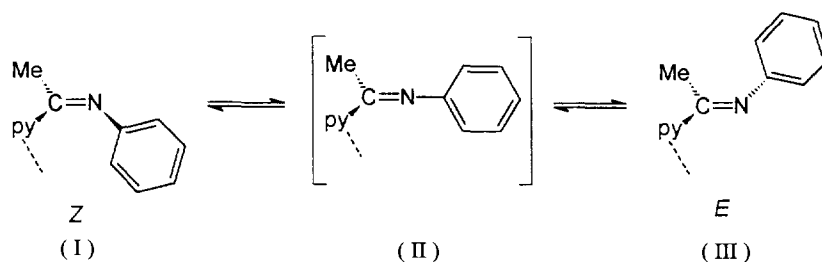
Fig. 6. 282.34 MHz ^{19}F NMR spectra (*meta* and *para* fluorines of C_6F_5 rings) of *cis*-[Pd(C_6F_5)$_2$(BIP)] in (CDCl$_2$)$_2$ showing the effects of the 1,4 metallotropic shift.

energies of similar magnitude. This means that the *E,Z* isomer is fully converted to the *E,E* isomer prior to its undergoing the 1,4 metallotropic shift. Scheme 4 represents the possible N inversion mechanism for this isomerisation process. In solution the structures represented in (I) and (III) are ground states, with the pendant imine in the *Z* or *E* configuration respectively. In the transition state (II) the unit C=N–C$_{ipso}$ is linear, consequently there is an sp hybridised N atom. The greater the electrophilicity of the metal, the lower the energy required to hybridise the N atom. The barrier to inversion is therefore likely to be affected by the electrophilicity of the metal due to the conjugated system between the donor atoms. This appears to be the case since, for the Pd(II) complex, the isomerisation energy barrier $\Delta G^{\neq}$ is 71.6 kJ mol^{-1} compared with 89.6 kJ mol^{-1} for the Pt(II) complex (see later). Below-ambient temperature spectroscopic studies were undertaken to investigate any restricted rotations in the major isomers of the complexes *cis*-[M(C$_6$F$_5$)$_2$(*E,E*-BIP)] (M = Pd or Pt). ^{1}H NMR spectra were recorded in CD$_2$Cl$_2$ solvent in the temperature range ambient to -85°C. On cooling, the *ortho* and *meta* signals of the phenyl ring attached to the coordinated nitrogen split into two magnetically inequivalent signals with equal intensity. No changes were observed for the phenyl ring in the pendant part of the BIP ligand. In the ^{19}F NMR spectra signals of the isochronous pairs of *ortho* and *meta* nuclei of each C$_6$F$_5$ ring split into distinct pairs of signals on cooling.

There are several potential bond rotation processes that a priori may possibly be restricted in these complexes, namely C–C rotation of the pendant part of the BIP ligand, M–C$_{ipso}$ rotation of each one of the C$_6$F$_5$ rings, and N–C$_{ipso}$ rotation of the phenyl ring attached to the metal-bound nitrogen. The dynamics of the bond

Scheme 3.

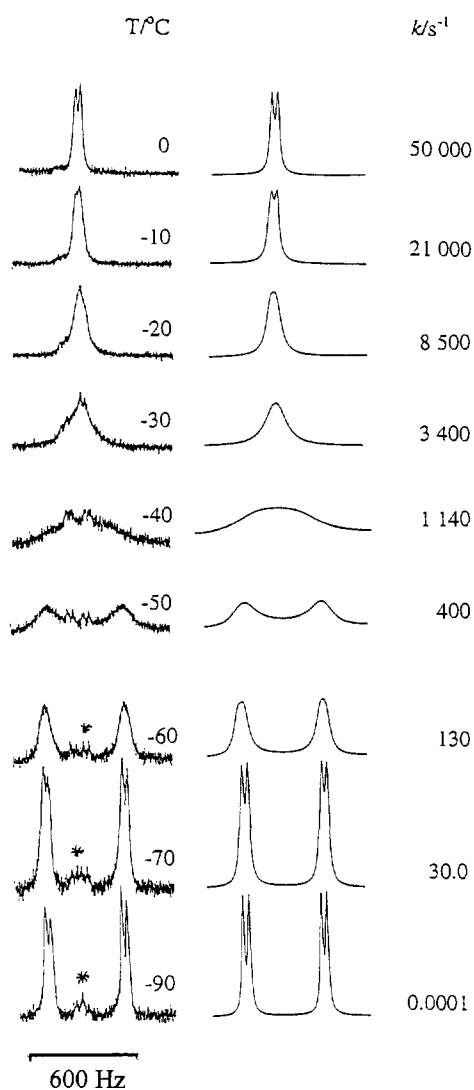Scheme 4.

T/°C   k/s⁻¹

0   50 000

-10   21 000

-20   8 500

-30   3 400

-40   1 140

-50   400

-60   130

-70   30.0

-90   0.0001

600 Hz

Fig. 7. 282.34 MHz ^{19}F NMR spectra (*ortho* fluorine signals F_6 and F_{10}) of cis-[Pd(C$_6$F$_5$)$_2$(BIP)] in CD$_2$Cl$_2$ in the low temperature range −90 to 0°C showing the effects of the restricted C–C rotation of the pendant E,E imine moiety. Asterisk indicates impurity signals.

rotation process(es) were probed by bandshape analysis. The complex [Pd(C$_6$F$_5$)$_2$(E,E-BIP)] was first investigated. The *ortho* and *meta* fluorines of each C$_6$F$_5$ ring broadened and split on cooling to give equal intensity pairs of multiplets. It was found that bandshape changes of both C$_6$F$_5$ rings could be theoretically simulated using the same set of rate constants. Good quality fittings were obtained when allowance was made for three-bond scalar F–F couplings. The spectra of the *ortho* fluorines F_6 and F_{10} (see Table 4) are shown in Fig. 7. The rates of rotation for [Pt(C$_6$F$_5$)$_2$(E,E-BIP)] were derived by the coalescence method using the signals of the *ortho* phenyl hydrogens which coalesced at 263 K.

The observation that the ^{19}F signals of the *ortho* and *meta* fluorines of each C$_6$F$_5$ ring and the *ortho* hydrogens of the metal-bound C$_6$H$_5$ ring are sensitive to the same magnitude of exchange rate constant at any given temperature strongly implies that the process causing these changes must be associated with another part of the complex, namely the pendant part of the BIP ligand, i.e. –C(CH$_3$)=NPh. Models suggest that rotation about the C–C bond linking the imine substituent to the pyridyl ring is likely to be restricted, with the preferred conformers being those where the plane containing the C=N–C atoms is orthogonal to the M^{II}N$_2$ plane. Two such conformers are possible, but these will be NMR indistinguishable because of the absence of (different) axial ligands attached to M^{II}. This explains the observed changes at low temperature of the *ortho* and *meta* (but not the *para*) ring fluorine nuclei of the C$_6$F$_5$ and metal-bound C$_6$H$_5$ ring. It does, however, presuppose that these rings are effectively locked in orthogonal conformations on the NMR timescale at the lowest temperatures.

This conclusion is very analogous to that reached for the low temperature conformations of the complexes [(M(C$_6$F$_5$)$_2$(terpy)] (M = Pd^{II} or Pt^{II}), where similar

Table 5
Activation parameters for fluxional processes in cis-[M(C$_6$F$_5$)$_2$(BIP)] (M = Pd or Pt) complexes

Compound	Process	Nucleus studied	T range (°C)	E_a (kJ mol⁻¹)	log (A (s⁻¹))	ΔH^* (kJ mol⁻¹)	ΔS^* (J mol⁻¹ K⁻¹)	ΔG^* ᵃ (kJ mol⁻¹)
	(i)	^{1}H	70–110	89.22 ± 0.81	12.7 ± 0.1	85.92 ± 0.78	−12.3 ± 2.0	89.59 ± 0.20
[Pt(C$_6$F$_5$)$_2$(BIP)]	(ii)	^{1}H	70–110	81.29 ± 0.58	11.9 ± 0.1	78.20 ± 0.57	−28.2 ± 1.5	86.60 ± 0.12
	(iii)	^{1}H	−80–20	—	—	—	—	47.43 ᵇ
	(i)	^{1}H	30–110	81.58 ± 1.25	14.5 ± 0.2	78.71 ± 1.27	23.8 ± 3.7	71.62 ± 0.18
[Pd(C$_6$F$_5$)$_2$(BIP)]	(ii)	^{1}H	60–110	—	—	—	—	70.42 ᶜ
	(iii)	^{19}F	−80–0	48.28 ± 0.41	13.9 ± 0.1	46.3 ± 0.40	15.1 ± 1.7	41.84 ± 0.11

(i) 1,4 Metallotropic shift; (ii) E,Z isomerisation; (iii) C–C restricted rotation of the pendant part of the BIP complex.
ᵃ At 298.15 K.
ᵇ Measured by coalescence temperature, T_c = 263 K.
ᶜ Measured by coalescence temperature, T_c = 393 K.

changes in the C_6F_5 *ortho* and *meta* fluorine signals were attributed to the varying rates of restricted rotation of the pendant pyridyl ring [9].

It will be noted in Table 5 that the entropies of activation are negative for the Pt complex and positive for the Pd complex. It is the authors' view that this does not reveal any significant difference in the dynamics of the two complexes. $\Delta S^{\neq}$ parameters can be measured precisely only when bandshape fittings can be made over a wide temperature range (i.e. $> 50\,°C$). The temperature range for fittings of the Pt complex was much more restricted than that for the Pd complex, so the $\Delta S^{\neq}$ parameters for the two complexes have different associated uncertainties, making comparison between them not very meaningful.

3. Discussion

Activation energy data were calculated from the derived rate constants and are shown in Table 5.

The difference in $\Delta G^{\neq}$ values for the metallotropic shift suggests that electronic and geometric factors contribute to the energy associated with the formation of the quasi-terdentate transition state. Magnitudes of $\Delta G^{\neq}$ are very comparable with those obtained for the analogous terpy complexes, being 71.6 compared with $71.0\,kJ\,mol^{-1}$ for the Pd^{II} complexes, and 89.6 compared with $93.9\,kJ\,mol^{-1}$ for the Pt^{II} complexes (Table 6). Energy barriers for E,Z isomerisation are of very similar magnitude to those of the 1,4 metallotropic shift, suggesting that both processes are concerted as discussed earlier. Magnitudes of $\Delta G^{\neq}$ for the C–C restricted rotation of the pendant part of the BIP ligand are markedly lower (by $30–40\,kJ\,mol^{-1}$) than the corresponding values for the 1,4 metallotropic shift (Table 5). The difference in values between Pd(II) and Pt(II) complexes is probably a result of steric interactions rather than the electrophilicity of the metal centres, with the larger size of Pt(II) causing more steric hindrance to rotation than Pd(II). Notably, the difference in $\Delta G^{\neq}$ values for these two metals is comparable with that found for the terpy complexes (where for Pd(II) $\Delta G^{\neq} = 47.0$ and for Pt(II) $\Delta G^{\neq} = 55.9\,kJ\,mol^{-1}$) [9]. This is

Table 6
$\Delta G^{\neq}$ [a] values for the 1,4 metallotropic shift of the ligand L in the complexes cis-[M(C_6F_5)$_2$L] (M = Pd or Pt; L = 2,6-disubstituted pyridine)

2,6-Substituent	M	$\Delta G^{\neq}$ $(kJ\,mol^{-1})$	Source
1-phenyliminoethyl	Pd	71.62 ± 0.18	This work
1-phenyliminoethyl	Pt	89.59 ± 0.20	This work
pyridyl	Pd	71.0 ± 0.2	[9]
pyridyl	Pt	93.9 ± 0.7	[9]

[a] Measured at 298.15 K.

expected since the geometric disposition of the metal centre should change consistently according to the ligand bound to it; i.e. the restriction to rotation should be dependent on the geometric disposition of the $M(C_6F_5)_2$ moiety.

4. Experimental

4.1. Physical measurements

Melting points were recorded in air on a Gallenkamp melting point apparatus and are uncorrected. Infrared spectra were recorded as CsI discs on a Nicolet Magna-IR 550 spectrometer calibrated from the $1602\,cm^{-1}$ signal of polystyrene. NMR spectra were recorded either on a Bruker AC300 spectrometer operating at 300.13 MHz for ^1H and at 282.34 MHz for ^{19}F or on a Bruker DRX400 spectrometer operating at 400.13 MHz for ^1H studies. ^1H chemical shifts are quoted relative to Me_4Si (TMS) and ^{19}F chemical shifts are quoted relative to C_6F_6 as internal standards. 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 to be accurate to $\pm 1\,°C$. Kinetic data were derived from bandshape analysis of either ^1H or ^{19}F NMR spectra using a version [21] of the standard DNMR program [22]. Activation parameters were calculated from a least-squares fit of the Arrhenius and Eyring plots. Quoted errors are statistical errors based on scattering of the rate constants around the straight line only.

4.2. Materials

The ligand 2,6-bis[1-(phenylimino)ethyl]pyridine (BIP) was prepared by condensation of 2,6-diacetyl-pyridine with aniline in benzene [23]. The compounds [Pd(C_6F_5)$_2$(diox)$_2$], cis-[PtCl$_2$(Et$_2$S)$_2$], and cis-[Pt(C_6F_5)$_2$(Et$_2$S)$_2$] were prepared by previous methods [1,24,25].

4.2.1. cis-[Pd(C_6F_5)$_2$(BIP)]

The complex [Pd(C_6F_5)$_2$(diox)$_2$] (0.09 g, 0.14 mmol) and BIP (0.05 g, 0.16 mmol) were stirred in 1,4-dioxane (50 cm^3) for 30 h. The solvent was reduced to approximately 10 cm^3, hexane (30 cm^3) was added and the solid obtained was washed with boiling hexane (3 × 30 cm^3) to afford a cream coloured powder. Yield 0.047 g, 39.0%.

4.2.2. cis-[Pt(C_6F_5)$_2$(BIP)]

The complex cis-[Pt(C_6F_5)$_2$(Et$_2$S)$_2$] (0.10 g, 0.14 mmol) and BIP (0.06 g, 0.19 mmol) were heated

under reflux in benzene (10 cm^3) for 30 h. After filtration, diethylether (20 cm^3) and hexane (20 cm^3) were added to the solution and it was cooled to approximately 20 °C. The solid obtained was washed with boiling hexane (2 × 30 cm^3), affording a bright yellow powder. Yield 0.05 g, 42.1%.

Acknowledgements

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