Synthesis and reactivity towards some weak, protic acids of the di-μ-hydroxo-bis[bis(2,4,6-trifluorophenyl)palladate(II)] ion

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Abstract

The reaction of *cis*-[Pd(C$_6$F$_3$H$_2$)$_2$(PhCN)$_2$] with 20% aqueous QOH (Q = NBu$_4$) in acetone leads to the formation of the hydroxo complex Q$_2$[{Pd(C$_6$F$_3$H$_2$)$_2$(μ-OH)}$_2$] (**1**). Complex **1** reacts with weak acids H(LL) in a 1:2 molar ratio to give Q$_2$[{Pd(C$_6$F$_3$H$_2$)$_2$(μ-LL)}$_2$] (LL = pyrazolate (pz) (**2**); 3-methylpyrazolate (mpz) (**3**); 3,5-dimethylpyrazolate (dmpz) (**4**); indazolate (indz) (**5**)) or Q[Pd(C$_6$F$_3$H$_2$)$_2$(LL)] (LL = acetylacetonate (acac) (**6**); benzoylacetonate (bzac) (**7**); 8-hydroxy-quinoline (oxin) (**8**)). Q$_2$[{Pd(C$_6$F$_3$H$_2$)$_2$}$_2$(μ-OH)(μ-dmpz)] (**9**) has been obtained by treatment of Q$_2$[{Pd(C$_6$F$_3$H$_2$)$_2$(μ-Cl)}$_2$] with QOH and Hdmpz (1:2:1 molar ratio) in methanol. Partial elemental analyses, conductance measurements and spectroscopic (IR, ^{1}H and ^{19}F NMR) methods have been used to study the new compounds.

Introduction

Bryndza and Tam in their extensive and well documented review [1] point out the recent surge of interest in the chemistry of the late transition-metal hydroxides, which is related to their interesting reactivity and potential relevance to catalysis. Synthetic routes used to prepare monomeric hydroxo complexes of the nickel group elements include metal exchange [2, 3], oxidative addition [4] and σ-ligand metathesis [3, 5–10] reactions. Similar methods have also been applied to the synthesis of non-organo-metallic hydroxo complexes of palladium and platinum [11, 12].

On the other hand, the labile complexes *cis*-[MR$_2$(PhCN)$_2$] (R = C$_6$F$_5$ (M = Ni or Pd) or C$_6$F$_3$H$_2$ (M = Pd)) have been shown to be convenient precursors for the preparation of other polyfluorophenyl complexes [13–15] including the hydroxo-bridged binuclear anionic [{M(C$_6$F$_5$)$_2$(μ-OH)}$_2$]$^{2-}$ (M = Ni or Pd) [16].

The work described herein shows that *cis*-[Pd(C$_6$F$_3$H$_2$)$_2$(PhCN)$_2$] may be used as a precursor to synthesize [{Pd(C$_6$F$_3$H$_2$)$_2$(μ-OH)}$_2$]$^{2-}$. The subsequent treatment of this hydroxo complex with the above-mentioned weak acids leads to the formation of the new trifluorophenyl–palladium derivatives

[{Pd(C$_6$F$_3$H$_2$)$_2$(μ-LL)}$_2$]$^{2-}$ and [Pd(C$_6$F$_3$H$_2$)$_2$(LL)]$^-$, depending on the identity of the (LL)$^-$ ligand.

Experimental

Instrumentation and starting materials

C, H and N analyses were carried out with a Perkin-Elmer 240C microanalyser. Conductivities were measured with a Philips PW 9501/01 conductimeter. Melting points were determined on a Reichert microscope. IR spectra were recorded on a Perkin-Elmer 1430 spectrophotometer and NMR spectra on a Varian FT-80A (^{19}F) or a Bruker AC 200E (^{1}H) instrument.

The complexes *cis*-[Pd(C$_6$F$_3$H$_2$)$_2$(PhCN)$_2$] and [NBu$_4$]$_2$[{Pd(C$_6$F$_3$H$_2$)$_2$(μ-Cl)}$_2$] were prepared as described elsewhere [15] and all the solvents were dried by literature methods before use.

Preparations

[NBu$_4$]$_2$[{Pd(C$_6$F$_3$H$_2$)$_2$(μ-OH)}$_2$] (1)

A 20% aqueous solution of [NBu$_4$]OH (0.228 ml; 0.174 mmol) was added to an acetone (10 ml) solution of *cis*-[Pd(C$_6$F$_3$H$_2$)$_2$(PhCN)$_2$] (100 mg; 0.174 mmol). After 30 min with constant stirring, the solution was concentrated under reduced pressure until a white solid began to precipitate. The addition of water–hexane (2:1) caused the complete precipitation

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of white crystals of complex 1, which were filtered off, washed with hexane and dried in the air.

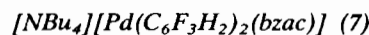*[NBu₄]₂[{Pd(C₆F₃H₂)₂(μ-LL)}₂] (LL = pz (2), mpz (3), indz (5))*
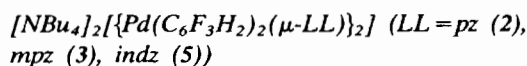
H(LL) (0.158 mmol) was added to a solution of complex 1 (100 mg; 0.079 mmol) in acetone (10 ml) and the mixture was stirred at room temperature for 30 min. The solution was then concentrated under reduced pressure to *c.* 2 ml. The addition of ethanol–water (1:1) caused the formation of white crystals of the corresponding azolate complex, which were collected by filtration, washed with ethanol and dried in the air.
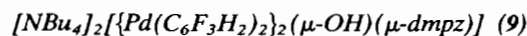
[NBu₄]₂[{Pd(C₆F₃H₂)₂(μ-dmpz)}₂] (4)
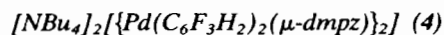
3,5-Dimethylpyrazole (100 mg; 0.158 mmol) was added to an ethanol (5 ml) solution of complex 1 (100 mg; 0.079 mmol). The mixture was stirred for 30 min and then vacuum-evaporated to dryness. The residue was extracted with dichloromethane (*c.* 3 ml) and the addition of hexane–ethanol (1:1) caused the precipitation of white crystals, which were separated by filtration, washed with ethanol and dried in the air.

[NBu₄][Pd(C₆F₃H₂)₂(LL)], LL = acac (6) or oxin (8)
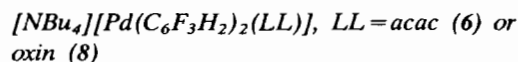
The corresponding protonated ligand (0.158 mmol of Hacac or Hoxin) was added to a solution of complex 1 (100 mg; 0.079 mmol) in acetone (10 ml) and the mixture was stirred for 30 min, then concentrated under reduced pressure to *c.* 2 ml. The addition of water (6) or ethanol (8) caused the precipitation of a white (6) or yellow (8) solid which was filtered off, washed with ethanol and dried in the air.

[NBu₄][Pd(C₆F₃H₂)₂(bzac)] (7)

Benzoylacetone (25.8 mg; 0.158 mmol) was added to a solution of complex 1 (100 mg; 0.079 mmol) in acetone (10 ml) and the mixture was stirred for 30 min. The solvent was evaporated to dryness and the residue was extracted with the minimum amount of ethanol–diethyl ether (1:1). The addition of hexane resulted in the precipitation of a white solid which was filtered off, washed with hexane and dried in the air.

[NBu₄]₂[{Pd(C₆F₃H₂)₂}₂(μ-OH)(μ-dmpz)] (9)

A 20% aqueous solution of [NBu₄]OH (0.140 mmol) was added to a methanol (7 ml) solution of 3,5-dimethylpyrazole (0.070 mmol). After 10 min with constant stirring, [NBu₄]₂[{Pd(C₆F₃H₂)₂(μ-Cl)}₂] (0.070 mmol) was added and the solution was stirred
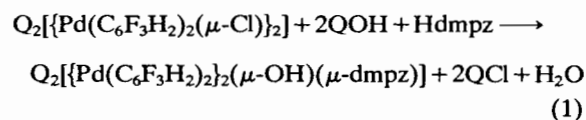
at room temperature for 1 h. The solvent was then partly evaporated under vacuum and water was added until precipitation of a white solid, which was separated by filtration and dried in the air.

Analytical data, yields, decomposition temperatures, and molar conductances for all the complexes are listed in Table 1.

Results and discussion

The results of our study are summarized in Scheme 1. The benzonitrile in *cis*-[Pd(C₆F₃H₂)₂(PhCN)₂] is readily displaced by the anionic ligand OH⁻ to give the hydroxo complex 1. The reaction occurs smoothly in acetone solution and complex 1 is isolated by precipitation with water–hexane.

Research on coordination chemistry of pyrazole-derived ligands has progressed rapidly in recent years and numerous double pyrazolate-bridged bimetallic complexes are known [18]. Complex 1 reacts with weak acids H(LL) (H(LL) = pyrazole (Hpz); 3-methylpyrazole (Hmpz); 3,5-dimethylpyrazole (Hdmpz); indazole (Hindz)) in 1:2 molar ratio to yield the corresponding di-μ-LL complexes Q₂[{Pd(C₆F₃H₂)₂(μ-LL)}₂] (LL = pz (2), mpz (3), dmpz (4), indz (5)) with the concomitant release of water. However, the analogous reaction with H(LL) = acetylacetone (Hacac), benzoylacetone (Hbzac) or 8-hydroxiquinoline (Hoxin) leads to the formation of the corresponding mononuclear anionic derivatives Q[Pd(C₆F₃H₂)₂(LL)] (LL = acac (6), bzac (7), oxin (8)) containing (LL)⁻ as a chelating bidentate ligand. All attempts made to prepare μ-hydroxo-μ-azolate complexes by reaction of complex 1 with H(LL) in a 1:1 molar ratio led to mixtures of the μ-OH-μ-LL and di-μ-LL complexes. The μ-OH-μ-dmpz complex 9 (Scheme 1) could be prepared by treating the di-μ-chloro complex with QOH and dimethylpyrazole under the appropriate conditions (eqn. (1)).

$$Q_2[\{Pd(C_6F_3H_2)_2(\mu\text{-}Cl)\}_2] + 2QOH + Hdmpz \longrightarrow$$

$$Q_2[\{Pd(C_6F_3H_2)_2\}_2(\mu\text{-}OH)(\mu\text{-}dmpz)] + 2QCl + H_2O \tag{1}$$

However, mixtures of the μ-OH-μ-LL and di-μ-LL complexes were again obtained when this method was applied to other azoles.

The IR spectra for all the isolated complexes exhibit the characteristic bands of the 2,4,6-C₆F₃H₂ group [15, 17] at *c.* 1605m, 1580s, 1395s, 1275m, 1140m, 1090s, 990vs and 803s-m cm⁻¹. The absorption at 830 cm⁻¹ appears to be similar to that found at *c.* 800 cm⁻¹ in square-planar bis(pentafluoro-

TABLE 1. Analytical results, yields, melting points, conductances and IR data

Complex[a]	Analysis (%)[b]			Yield (%)	m.p.[c] (°C)	$\Lambda_M{}^d$	Relevant IR bands (Nujol; cm^{-1})	
	C	H	N				X-sensitive	Others
$Q_2[\{Pd(C_6F_3H_2)_2(\mu\text{-OH})\}_2]$ (1)	53.7 (53.6)	6.4 (6.6)	2.3 (2.2)	90	170	165	840, 830	OH str: 3620
$Q_2[\{Pd(C_6F_3H_2)_2(\mu\text{-pz})\}_2]$ (2)	54.9 (54.9)	6.6 (6.4)	5.8 (6.2)	84	215	208	815sh	pz: 1060, 750, 640
$Q_2[\{Pd(C_6F_3H_2)_2(\mu\text{-mpz})\}_2]$ (3)	55.4 (55.5)	6.7 (6.6)	5.8 (6.1)	72	217	217	810, 825	mpz: 1065, 740
$Q_2[\{Pd(C_6F_3H_2)_2(\mu\text{-dmpz})\}_2]$ (4)	55.9 (56.1)	6.5 (6.7)	5.6 (5.9)	78	220	193	825br	dmpz: 1520, 1035, 750
$Q_2[\{Pd(C_6F_3H_2)_2(\mu\text{-indz})\}_2]$ (5)	57.4 (57.7)	6.1 (6.2)	5.3 (5.8)	75	209	230	840, 825	indz: 1200, 910, 800, 760
$Q[Pd(C_6F_3H_2)_2(acac)]$ (6)	56.0 (55.8)	7.0 (6.7)	1.9 (2.0)	87	148	109	840, 830	acac: 1545, 1510, 1400, 420
$Q[Pd(C_6F_3H_2)_2(bzac)]$ (7)	58.9 (59.0)	6.3 (6.5)	2.1 (1.8)	81	179	102	840sh, 830	bzac: 1560, 1510, 1395, 450, 425
$Q[Pd(C_6F_3H_2)_2(oxin)]$ (8)	58.3 (58.8)	6.2 (6.3)	4.1 (3.7)	82	153	94	835, 820	oxin: 1560, 1400, 800, 785
$Q_2[\{Pd(C_6F_3H_2)_2\}_2(\mu\text{-OH})(\mu\text{-dmpz})]$ (9)	54.6 (54.9)	6.7 (6.6)	4.8 (4.2)	70	168	179	810sh, 820	dmpz: 1520, 1030, 740 OH str: 3600

[a]$Q = NBu_4$. [b]Calculated values in parentheses. [c]All compounds decompose. [d]In Ω^{-1} cm^2 mol^{-1} (solvent acetone, $c \approx 5 \times 10^{-4}$ M).
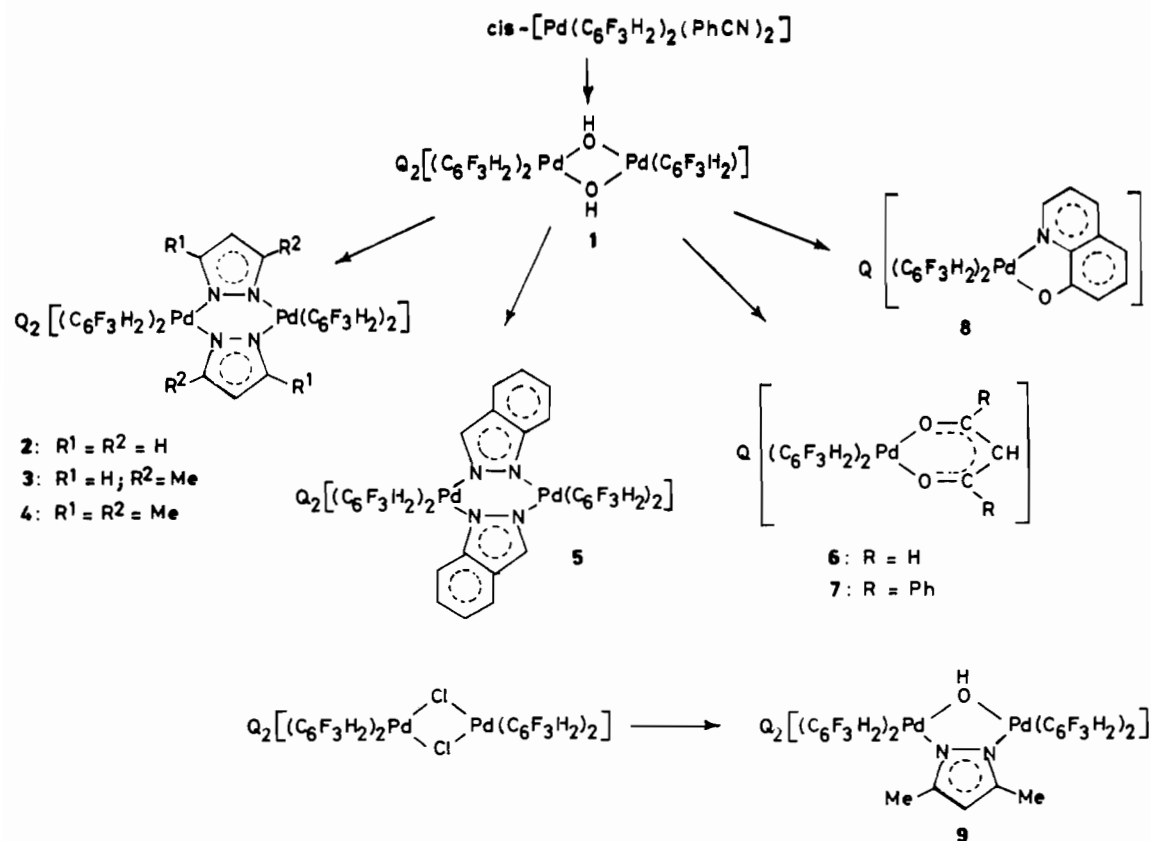

Scheme 1. Synthesis of the trifluorophenyl derivatives of palladium(II) (Q=NBu₄).

TABLE 2. ^{1}H and ^{19}F NMR data (J in Hz)

Complex	^{1}H, δ (ppm)[a] (reference SiMe$_4$)	^{19}F, δ (ppm) (reference CFCl$_3$)	
		F$_o$	F$_p$
1[b]	6.06 (dd, 8H, C$_6$F$_3$H$_2$, J_{HFp} 9.9, J_{HFo} 4.8) −2.94 (s, 2H, OH)	−81.06	−122.64
2[b]	7.07 (d, 4H, 3- and 5-H of pz, J 1.8) 6.11 (d, 8H, C$_6$F$_3$H$_2$, J_{HFp} 10) 5.59 (t, 2H, 4-H of pz, J 1.8)	−82.70	−122.64
3[b]	7.42 (d, 2H, 5-H of mpz, J 1.6) 6.0 (br, 8H, C$_6$F$_3$H$_2$) 5.36 (d, 2H, 4-H of mpz, J 1.6) 1.86 (s, 6H, CH$_3$)	−74.78 −79.68 −81.54	−123.76
4[b]	6.01 (d, 8H, C$_6$F$_3$H$_2$, J_{HFp} 10.1) 5.06 (s, 2H, 4-H of dmpz) 2.15 (s, 12H, CH$_3$)	−73.05	−124.47
5[b]	8.16 (s, 2H, 3-H of indz) 7.64 (d, 2H, 7-H of indz, J 8.3) 7.60 (d, 2H, 4-H of indz, J 7.9) 6.60 (pseudotriplet, 2H, 6-H of indz) 6.51 (pseudotriplet, 2H, 5-H of indz) 6.4 (br, 2H, C$_6$F$_3$H$_2$) 6.1 (br, 4H, C$_6$F$_3$H$_2$) 5.9 (br, 2H, C$_6$F$_3$H$_2$)	−77.04 −81.34 −82.91	−123.71
6[c]	6.11 (dd, 4H, C$_6$F$_3$H$_2$, J_{HFp} 10, J_{HFo} 5.0) 5.17 (s, 1H, CH) 1.78 (s, 6H, CH$_3$)	−84.17	−120.78
7[c]	7.68 (m, 2H, 2- and 6-H of Ph) 7.24 (m, 3H, 3-, 4- and 5-H of Ph) 6.20 (dd, 4H, C$_6$F$_3$H$_2$, J_{HFp} 9.7, J_{HFo} 5.3)	−84.65 −84.88	−120.91
8[c]	7.98 (d, 1H, 2-H of oxin, J 8.0) 7.58 (d, 1H, 7-H of oxin, J 4.9) 7.0 (m, 2H, 3- and 6-H of oxin) 6.69 (d, 2H, 4- and 5-H of oxin, J 8.1) 6.20 (m, 4H, C$_6$F$_3$H$_2$)	−83.19 −83.91	−120.10 −120.67
9[b]	6.02 (m, 8H, C$_6$F$_3$H$_2$) 5.22 (s, 1H, 4-H of dmpz) 1.54 (s, 6-H, CH$_3$) −1.59 (s, 1H, OH)	−78.40 −79.09	−122.55 −123.66

[a]Additional peaks of [NBu$_4$]$^+$ are found at δ 3.2 (t, N-CH$_2$), 1.7 (m, CH$_2$CH$_2$CH$_2$), 1.5 (m, CH$_2$CH$_3$) and 1.0 (t, CH$_3$), with the correct intensity ratio. [b]Solvent (CD$_3$)$_2$CO. [c]Solvent CD$_3$Cl.
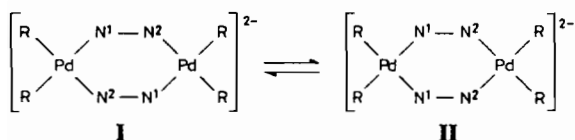
phenyl)palladium(II) derivatives [19] which is derived from the so-called 'X-sensitive' mode of the fluorophenyl ring [20]. In the trifluorophenyl derivatives reported herein this absorption is observed as a broad or split band (Table 1) which is consistent with the presence of the cis-Pd(C$_6$F$_3$H$_2$)$_2$ moiety [15]. The presence of the [NBu$_4$]$^+$ cation in all the complexes is manifested by two bands at 870 and 750 cm^{-1}. Some characteristic bands of the (LL)$^-$ ligands are listed in Table 1. Measurements of the molar conductivity in acetone solution (Table 1) indicate that the complexes behave as 2:1 (1–5 and 9) or 1:1

(6–8) electrolytes [21], in accordance with the proposed formulae.

The ^{1}H and ^{19}F NMR data are listed in Table 2. The high-field proton resonance of the OH bridges in complex 1 is consistent with its reactivity towards the weak protic electrophiles H(LL) to give complexes 2–8. This signal is shifted to low field when one OH bridge is replaced by dmpz, as shown by complex 9. On the other hand, the hydrogen atoms in the C$_6$F$_3$H$_2$ rings give the expected doublet (by coupling to the para-F atom) or doublet of doublets (by coupling to both the ortho- and para-F atoms), but

overlapping of these NMR patterns takes place in complexes 8 and 9. The azolate ligands in complexes 2–5 and 9 give proton NMR signals which are in agreement with the results reported for other μ-pyrazolate complexes [22, 23]. The ^{19}F NMR data are also consistent with the proposed structures. Thus complexes 1, 2, 4 and 6 show two 2:1 resonances for the *ortho-* and *para*-F atoms, respectively, but four 2:2:1:1 resonances are seen in the spectra of complexes 8 and 9. However, complex 7 gives three signals (intensity ratio 1:1:1) because the resonances of the two *para*-F atoms are coincident.

The NMR behaviour of complexes 3 and 5 deserves further comment. Three broad signals in the *ortho*-F region are observed in the room-temperature ^{19}F spectra of both compounds and the corresponding ^{1}H resonances of the $C_6F_3H_2$ rings are also broad signals (see Table 2). A recent variable-temperature ^{19}F NMR study [24] has demonstrated that the pentafluorophenyl analogues of complexes 3 and 5 exhibit a dynamic behaviour owing to the asymmetric nature of the mpz and indz ligands. If these ligands are represented by N^1–N^2, it is possible to describe complexes 3 and 5 as the result of a dynamic chemical process involving structures I–II, each containing two pairs of equivalent

$$\left[\begin{array}{c} R \diagdown \diagup N^1 - N^2 \diagdown \diagup R \\ Pd \qquad Pd \\ R \diagup \diagdown N^2 - N^1 \diagdown R \end{array}\right]^{2-} \rightleftharpoons \left[\begin{array}{c} R \diagdown \diagup N^1 - N^2 \diagdown \diagup R \\ Pd \qquad Pd \\ R \diagup \diagdown N^1 - N^2 \diagdown R \end{array}\right]^{2-}$$

$$\mathbf{I} \qquad\qquad\qquad \mathbf{II}$$

trifluorophenyl (R) rings. On this assumption, the appearance of the NMR spectra should be dependent on the interconversion rate compared with the NMR time-scale and the NMR data of Table 2 correspond to relatively slower interconversion rates. Figure 1 shows the ^{1}H NMR spectrum (indz and $C_6F_3H_2$ regions) of the indz complex recorded at different temperatures. Between -60 and 15 °C the spectra show three broad signals (in the range -60 to 0 °C the lower field signal is completely or partly overlapped with the higher-field indz signal) attributed to the hydrogen atoms of four different $C_6F_3H_2$ groups corresponding to structures I and II and the intensity ratio 2:4:2 indicates that two resonances are coincident. At 25 °C the signals are near the coalescence and at 35 °C the spectrum shows two broad signals (intensity ratio 4:4) because structures I and II become indistinguishable.

Acknowledgements
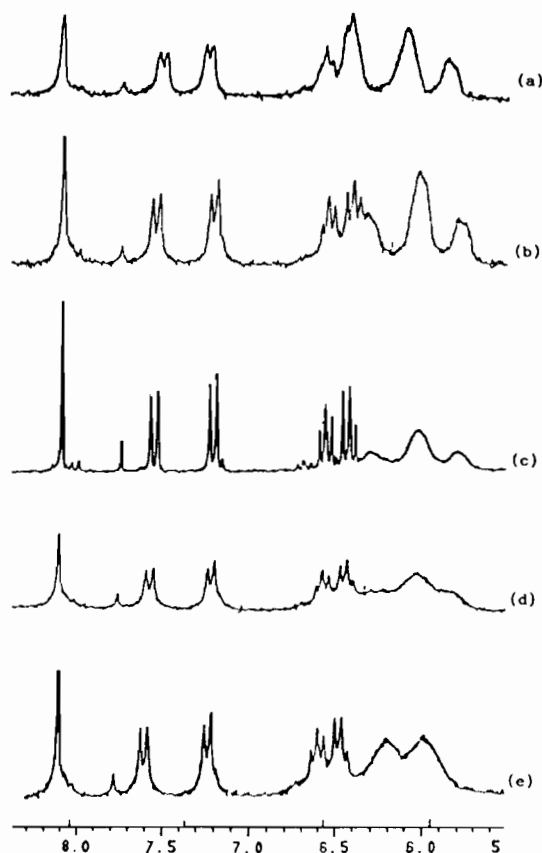
Fig. 1. ^{1}H NMR spectra of complex 5 in the indz and $C_6F_3H_2$ regions only at 200 MHz in $(CD_3)_2CO$ at temperatures of -60 (a), 0 (b), $+15$ (c), $+25$ (d) and $+35$ (e) °C. The spectra at -45, -30 and -15 °C are similar to (b).

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