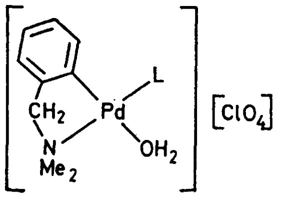
Dynamic Behaviour in Solution of Some Benzo[*h*]quinoline and 8-Methylquinoline Complexes of Palladium(II)†

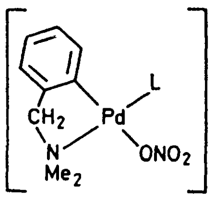
By **Antony J. Deeming** and **Ian P. Rothwell**, Department of Chemistry, University College, London, 20 Gordon Street, London WC1H 0AJ

Enantiomeric forms of [Pd(dmp)L(OH$_2$)][ClO$_4$] [dmp = 2-(dimethylaminomethyl)phenyl, L = benzo[*h*]quinoline (bquin) or 8-methylquinoline (8Me-quin)] rapidly interconvert in (CD$_3$)$_2$CO solution to give coalescence of the methyl ^{1}H n.m.r. singlets of the dmp ligand. A kinetic study of this process for L = bquin supports a unimolecular displacement of H$_2$O associated with the ligand L rotating from largely above to largely below the co-ordination plane. This is supported by the non-dynamic nature of [Pd(dmp)L(NO$_3$)]. Addition of small amounts of D$_2$O to the (CD$_3$)$_2$CO solution of [Pd(dmp)(bquin)(OH$_2$)][ClO$_4$] considerably reduces the rate of inversion, which probably results from a breakdown of the more reactive ion pairs.

We have previously described[1] the preparation of the complexes [Pd(dmp)L(OH$_2$)][ClO$_4$] (1) and [Pd(dmp)-L(NO$_3$)] (2) {dmp = 2-(dimethylaminomethyl)phenyl; L = benzo[*h*]quinoline (bquin) or 8-methylquinoline (8Me-quin)}. The structure of (1; L = bquin) in the crystal has been established[1] and the ligand L shown to adopt a configuration with the ligand plane perpendicular to the co-ordination plane. The Pd···H^{10} distance is short (2.09 Å) but is prevented from being even shorter by a tilt of the bquin ligand.[1] Hydrogen-1 n.m.r. spectra in (CD$_3$)$_2$CO for complexes (1) or in CDCl$_3$ for (2) are in every way consistent with structures in solution analogous to that for (1; L = bquin) in the crystal (Figure 1).



(1)



(2)

(L = bquin or 8Me—quin)

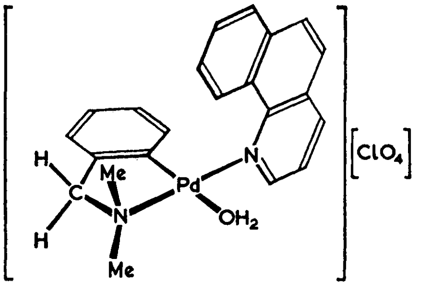


Figure 1 Structure of [Pd(dmp)(bquin)(OH$_2$)][ClO$_4$]

However, as described in this paper, complexes (1) but not (2) show dynamic behaviour in solution consistent with the rapid interconversion of enantiomers, which requires the bulk of the ligand L to move from above to below the co-ordination plane. Thus the NMe$_2$ group of the dmp ligand in [Pd(dmp)(bquin)(OH$_2$)]-[ClO$_4$] in dry (CD$_3$)$_2$CO solution at −20 °C gives two sharp singlets and likewise the NCH$_2$ group an AB quartet, but these signals coalesce to two sharp singlets on increasing the temperature. We have attempted to establish the mechanism of the process leading to these changes.

RESULTS

The rates of exchange ($k_{\text{exch.}}$) of the two enantiomeric forms of [Pd(dmp)(bquin)(OH$_2$)][ClO$_4$] were measured in (CD$_3$)$_2$CO solution at various temperatures (spectra 1—6, Table) by line-shape analysis of the NMe$_2$ signals (Figure 2). Corresponding broadening and coalescence of the AB quartet due to the NCH$_2$ protons were observed. The calculated coalescence temperature T_c(AB) for coalescence of the AB quartet using rate data obtained from the methyl signals is 25 °C. The experimental value of T_c(AB) is less precisely determined than that for the methyl singlets, partly because the signals are somewhat obscured by the water peak. Nevertheless, T_c(AB) is between 20 and

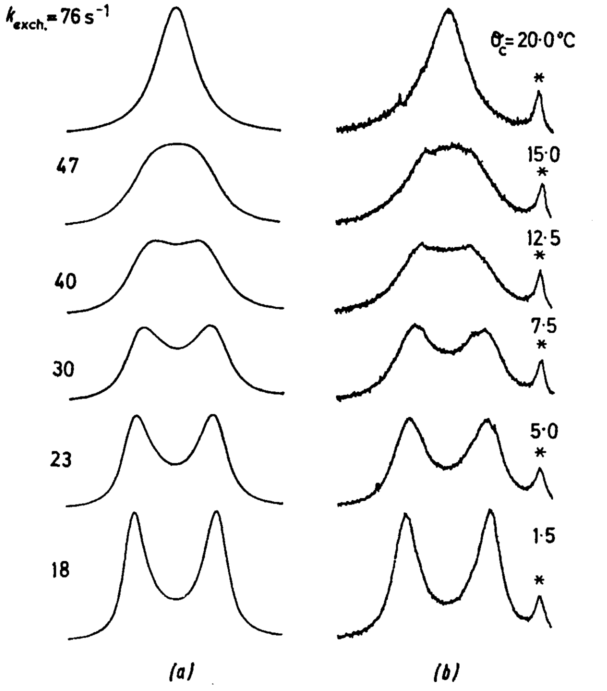


Figure 2 Hydrogen-1 n.m.r. spectra [(*a*) calculated, (*b*) observed] for the NMe$_2$ group of [Pd(dmp)(bquin)(OH$_2$)][ClO$_4$] in (CD$_3$)$_2$CO (0.264 mol dm^{-3}). The asterisked peak is due to [Pd(dmp)(OH$_2$)(sol)][ClO$_4$]

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† No reprints available.

[1] A. J. Deeming, I. P. Rothwell, M. B. Hursthouse, and L. New, preceding paper.

30 °C indicating that the protons of NCH_2 exchange at the same rate as those of NMe_2. An Arrhenius plot (Figure 3)

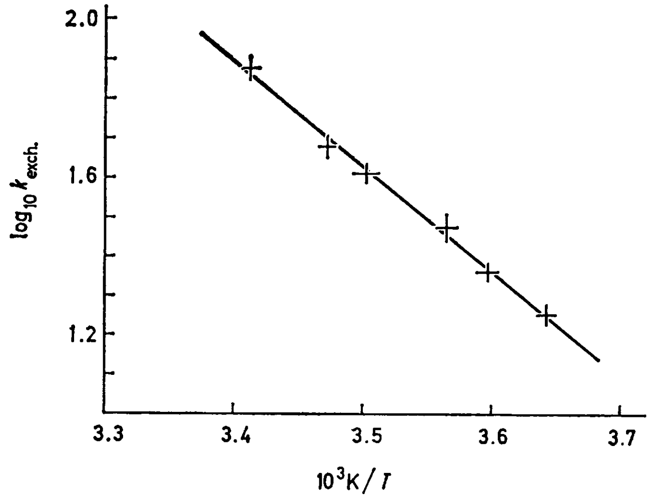

FIGURE 3 Arrhenius plot using values of $k_{exch.}$ derived from Figure 2

gave $E^{\ddagger} = 50 \pm 5$ kJ mol^{-1} and $A = 10^{10.8}$. Further results relating to the mechanism are as follows.

(*a*) $k_{exch.}$ is independent of the concentration of [Pd(dmp)(bquin)(OH_2)][ClO_4] (spectra 7—9, Table), but while this is a requirement for an intramolecular exchange it does not preclude other mechanisms.

Exchange rates $k_{exch.}$ for NMe_2 groups in [Pd(dmp)(bquin)(OH_2)][ClO_4] measured in dry $(CD_3)_2CO$ or with various amounts of D_2O added

Spectrum number	[complex]/ mol dm^{-3}	[D_2O]/ mol dm^{-3}	θ_c */°C	$k_{exch.}$/ s^{-1}
1	0.264 ± 0.004	0	20.0	76 ± 3
2	0.264 ± 0.004	0	15.0	47 ± 2
3	0.264 ± 0.004	0	12.5	40 ± 1
4	0.264 ± 0.004	0	7.5	30 ± 2
5	0.264 ± 0.004	0	5.0	23 ± 1
6	0.264 ± 0.004	0	1.5	18 ± 1
7	0.125 ± 0.003	0	15.0	48 ± 1
8	0.264 ± 0.004	0	15.0	47 ± 2
9	0.380 ± 0.005	0	15.0	48 ± 2
10	0.264 ± 0.004	0	20.0	74 ± 3
11	0.263 ± 0.004	0.239 ± 0.006	20.0	47 ± 1
12	0.262 ± 0.004	0.358 ± 0.012	20.0	40 ± 1
13	0.262 ± 0.004	0.406 ± 0.018	20.0	36 ± 1
14	0.261 ± 0.004	0.536 ± 0.024	20.0	31 ± 2
15	0.260 ± 0.004	0.771 ± 0.030	20.0	26 ± 1
16	0.258 ± 0.004	1.18 ± 0.04	20.0	20 ± 1
17	0.256 ± 0.004	1.75 ± 0.04	20.0	13 ± 1
18	0.101 ± 0.003	0.239 ± 0.006	20.0	46 ± 2
19	0.256 ± 0.004	0.239 ± 0.006	20.0	47 ± 1

* Error ±0.5 °C.

(*b*) Addition of free bquin to the solution at 30 °C, which is well above T_c, led to separate sharp signals for free and co-ordinated bquin. Hence the enantiomeric exchange process does not involve bquin dissociation from the complex since this would have led to a collapse of these ligand signals. The absence of a rapidly reversible dissociation of bquin is also supported by there being separate signals due to [Pd(dmp)(bquin)(OH_2)][ClO_4] and [Pd(dmp)(OH_2)(sol)][ClO_4] (sol = solvent; acetone here but water when this has been added to the solution) at 30 °C. The latter species is always present in low concentration in solution (see Figure 2), increasing somewhat on addition of water to the dry acetone solution, but exchange between these species is considerably slower than interchange between the enantiomers. Using the program TRIGEN/2 for the line-shape analysis of three exchanging species, we estimated the exchange rate of the bquin with the solvent species to be *ca.* 4 s^{-1} at 20 °C where $k_{exch.} = 76$ s^{-1}; this latter figure is unaltered by making allowance for exchange with the solvent species. It is unlikely that any process involving bquin dissociation would not also involve this disolvated species. Although free bquin does not exchange with co-ordinated bquin, its addition does increase the observed exchange rate slightly. On addition of 0.1 mol bquin per mol of complex the methyl exchange rate at 5 °C increased by less than a factor of two, smaller additions giving proportionally smaller effects. It may be that under these conditions a different (bimolecular) process operates in addition to the unimolecular process occurring in the absence of added bquin, but we have not examined this in any detail.

(*c*) The corresponding nitrato-complexes (2; L = bquin or 8Me-quin) do not show dynamic n.m.r. behaviour. Thus two sharp NMe_2 singlets and an AB quartet for NCH_2 were observed for (2; L = bquin) in $CDCl_3$ up to 60 °C. If it occurs at all, enantiomeric exchange is considerably slower than for the aqua-complexes (1).

(*d*) The addition of D_2O to a solution of (1; L = bquin) in $(CD_3)_2CO$ led to a considerable reduction in $k_{exch.}$ (spectra 10—17, Table and Figure 4). However, the value of $k_{exch.}$ is apparently controlled only by the concentration of D_2O and not the [complex] : [D_2O] ratio (spectra 11, 18, and 19; Table).

It was further observed that the chemical-shift separation ($\Delta\nu$) of the methyl singlets at −20 °C (well below T_c) is strongly dependent on the concentration of D_2O in $(CD_3)_2CO$, and Figure 5 shows the reduction of $\Delta\nu$ with increasing [D_2O] at three different complex concentrations. From Figures 4 and 5 it can be seen that $\Delta\nu$ and $k_{exch.}$ are similarly dependent on [D_2O] rather than [complex] : [D_2O] so that plots of one against the other (Figure 6) are linear and essentially parallel. Thus the reductions in $\Delta\nu$ and $k_{exch.}$ are *ca.* 50% complete when [D_2O] = 0.35 mol dm^{-3} whatever the complex concentration. We believe that $k_{exch.}$ and $\Delta\nu$ are both related to changes in the solution structure of the complex which depends on [D_2O] (see Discussion section). $\Delta\nu$ is only slightly dependent on [complex].

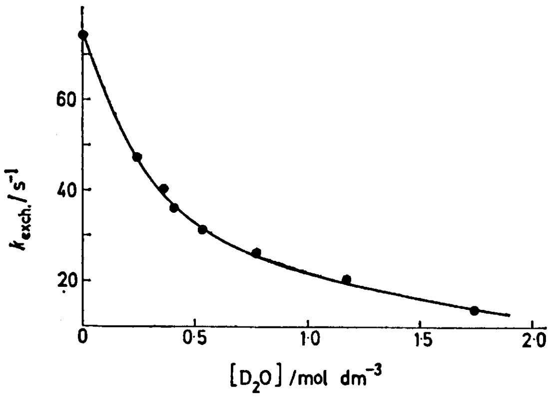

FIGURE 4 Plot of $k_{exch.}$ against [D_2O] for spectra 10—17 (Table)

DISCUSSION

For [Pd(dmp)(bquin)(OH_2)][ClO_4] the H^{10} signal in the ^1H n.m.r. spectrum is at δ 12.64 p.p.m. at −38 °C, the remarkably low shift being due to the paramagnetic anisotropy of the metal atom.[1] The greatest downfield shift is when the proton is perpendicularly above the metal atom and closest to it. It has been shown that free rotation, such as about the Pd–N(bquin) bond, would nullify this effect so that the proton shift would be much closer to that of the free ligand (δ 9.2 p.p.m.).[2] However this requires no preferred angle of orientation of bquin about this bond, while in our case with a sufficiently large rotational barrier the most populated conformation in solution should approximate to that in the crystal. Interconversion of enantiomers will not then in itself lead to any chemical shift change. Indeed, the only noticeable change in the bquin signals over the temperature range in which the NMe_2 signals are coalescing is a shift in the H^{10} signal from δ 12.64 (−38) to 12.54 p.p.m. (30 °C).

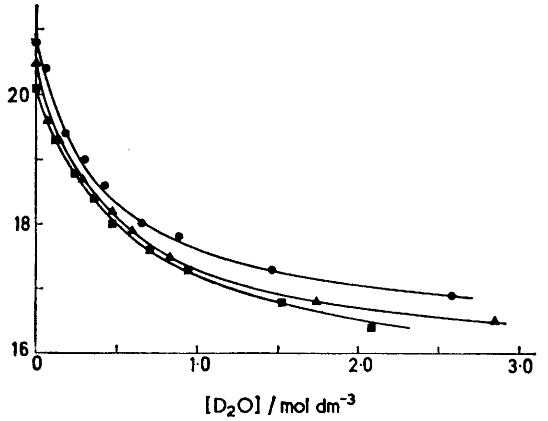

FIGURE 5 Plot of $\Delta\nu$, the chemical shift between the NMe_2 signals of [Pd(dmp)(bquin)(OH_2)][ClO_4] in $(CD_3)_2CO$ solution with added D_2O recorded at 100 MHz, against [D_2O] for the complex concentrations 0.139 (●), 0.203 (▲), and 0.368 mol dm^{-3} (■)

The Scheme shows possible mechanisms for the interconversion of the enantiomers. Mechanism (B) is ruled out because there is no exchange of free with co-ordinated bquin at the rate of enantiomer interconversion. Also we believe that a simple rotation about the Pd–N bond as in (A) is impossible. The Pd–O and Pd–C distances for the ligands *cis* to bquin are 2.20 and 1.94 Å respectively and the short Pd–H(bquin) distance (2.09 Å) prevents rotation of the bquin without prior loss of a ligand *cis* to it. The rapidly reversible chelate-ring opening (E) has no precedence in any of the other dmp complexes we have studied and so water dissociation as in (C) or (D) is favoured, and the specific involvement of water in the reaction is consistent with the lack of dynamic behaviour of the nitrato-complexes. In the crystal Pd–OH_2 is a particularly long bond (2.20 Å) compared with the other bonds to palladium (2.06, 2.06, and 1.94 Å) and the position of the H_2O *trans* to Pd–C may in part account for the good leaving ability of this ligand. The 'frozen-out' spectra show that only one bquin complex is present in solution so that any product of water dissociation must be in low concentration. (C) and (D) can be distinguished if (C) involves detachment of the dissociated water from the ions, in which case the concentration of the water-free complex and hence the rate of inversion would depend on the concentration of complex (1). The constant rate over the concentration range 0.125—0.385 mol dm^{-3} eliminates this possibility. Our results do not clearly define the nature of the water-free complex, but we tend to favour mechanism (D) in which each water dissociation leads to inversion *via* the intermediate (or transition state) which is formally three-co-ordinate with H^{10} of bquin occupying the fourth site.

Substituents on the ligands 8Me-quin or bquin which prevent their moving into the co-ordination plane should also prevent exchange. Thus the complex [Pd(dmp)-L(OH_2)][ClO_4] (L = 2,8-dimethylquinoline) does not show dynamic behaviour as when L = 8Me-quin. Separate sharp NMe signals (δ 2.98 and 3.01 p.p.m.) are detected even at 62 °C so that the 2Me group has quenched enantiomer exchange; an intermediate as in (D) would require severe collision of the 2Me group with H^2 of the dmp ligand. On the other hand, the 2Me group should enhance the rate if (B) operates and would be unlikely to affect the rate of chelate-ring opening as in (E). The corresponding nitrate [Pd(dmp)L(NO_3)] (L = 2,8Me_2-quin) is also non-dynamic.

The rate inhibition by added water (Figure 4) requires some comment, since this depends only on the composition of the D_2O–$(CD_3)_2CO$ mixtures implying a medium effect. In concentrated acetone solutions (0.1—0.4 mol dm^{-3}), as used in our n.m.r. studies, it is likely that ion pairing is significant and possibly even supported by hydrogen bonding between co-ordinated water and perchlorate. We were unable to measure conductances for solutions used for n.m.r. work but found that the molar conductances for considerably more dilute solutions of (1; L = bquin) in nitrobenzene are strongly concentration dependent [Λ/S cm^2 mol^{-1} at 20 °C for the

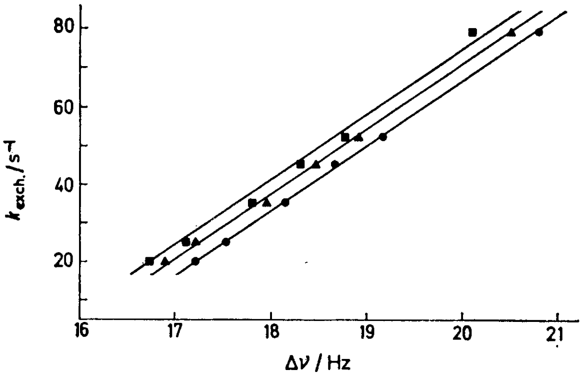

FIGURE 6 Plots of $k_{exch.}$ against $\Delta\nu$ derived from Figures 4 and 5

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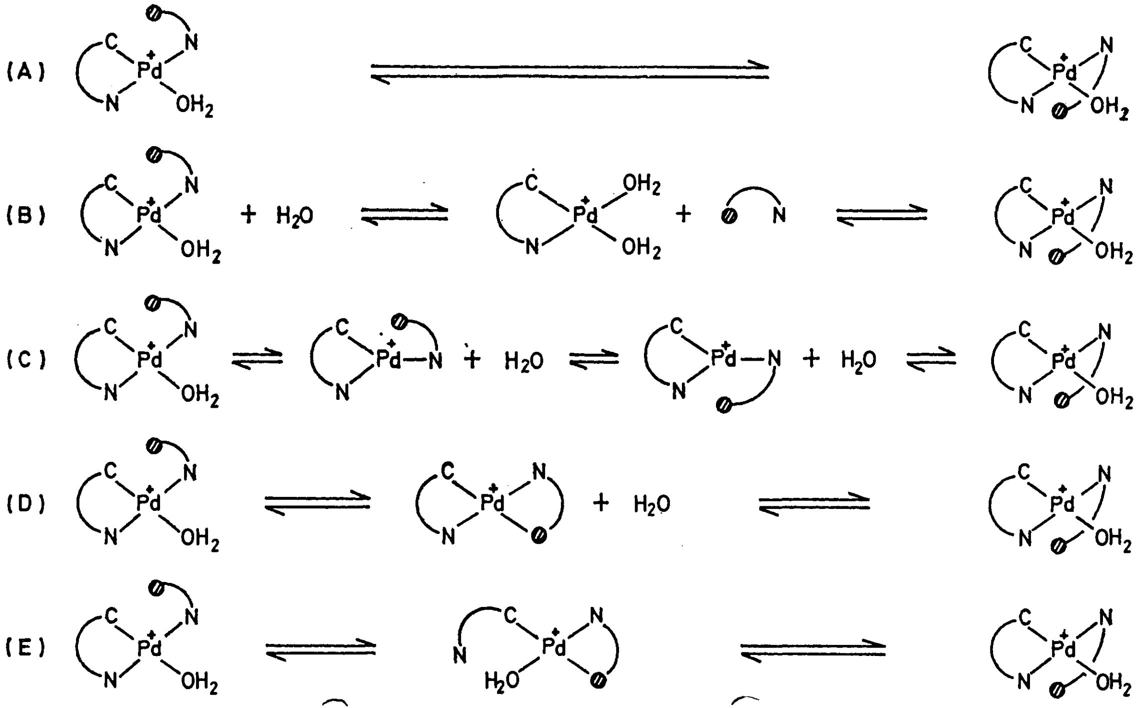
[2] R. G. Miller, R. D. Stauffer, D. R. Fahey, and D. R. Parnell, *J. Amer. Chem. Soc.*, 1970, **92**, 1511.

concentrations (mol dm^{-3}) given in parentheses = 12.8 (5.29×10^{-3}), 15.8 (2.65×10^{-3}), 21.6 (8.82×10^{-4}), 25.1 (2.65×10^{-4}), and 29.5 (6.61×10^{-5})].

The percentage of ion pairing increases with concentration so that the dry $(CD_3)_2CO$ solutions in the n.m.r. studies probably contained *ca.* 100% ion pairs which are characterised by high $\Delta\nu$ and high $k_{exch.}$. The addition of even small amounts of water might significantly modify the solute structure, and in particular lead to a breakdown of ion pairing. On this interpretation the rate of water dissociation from the complex is greater for the ion pair than when the ions are separated by water. A change of solute structure on adding water is strongly indicated by the results given in Figure 5. The linear relation between $\Delta\nu$ and $k_{exch.}$ shown in Figure 6 could indicate that changes in both these parameters are related to the same structural changes. The complexes of different structure in solution, whether the ion-pairing interpretation is correct or not, must be in very rapid dynamic equilibrium so that $k_{exch.}$ and $\Delta\nu$ are properties of the time-averaged structure in solution.



SCHEME $\widehat{C\ N}$ = 2-(dimethylaminomethyl)phenyl, $\widehat{\oslash\ N}$ = bquin

EXPERIMENTAL

The complex $[Pd(dmp)(bquin)(OH_2)][ClO_4]$ [1] was chosen for study because the chemical-shift separation of the methyl singlets ($\Delta\nu$) is 0.20 p.p.m., whereas the separation $\Delta\nu$ for the 8Me-quin analogue is 0.08 p.p.m. making kinetic measurements difficult. Solutions within the concentration range 0.1—0.4 mol dm^{-3} were prepared by dissolving weighed amounts of the complex in dry $(CD_3)_2CO$ and making up the solution to 0.460 ± 0.004 cm^3. The dryness of the solvent was indicated by the H_2O signal in the ^1H n.m.r. spectrum which has an intensity equivalent to two protons when integrated against the dmp signals; any free water would have added intensity to this signal. Spectra were recorded on a Varian HA100 spectrometer with temperature calibration (±0.5 °C) from the chemical shifts for MeOH. Experimental line shapes for the NMe_2 signals in the range 0—20 °C were matched against those calculated for different exchange rates $k_{exch.}$ using a DUBGEN/3 computer program. Spectral parameters (peak widths and positions) for the non-exchanging system were obtained from spectra at −20 °C. From the values of $k_{exch.}$ at different temperatures obtained in this way we calculated the activation parameters $E^{\ddagger}$ and A. The effect of added water on $k_{exch.}$ was studied by making incremental additions of D_2O from a microsyringe and recording the spectrum at 20 °C after each addition. To determine $k_{exch.}$ in this case it was necessary to vary the limiting low-temperature value of $\Delta\nu$ to obtain the best line-shape matching. This was because $\Delta\nu$ at −20 °C depends markedly on the water concentration, especially when this is low, and also on the temperature for a particular water concentration. There is little variation of $\Delta\nu$ with temperature in the absence of added water or with complex concentration under any circumstances; our explanations for this are in the Discussion section.

2,8-*Dimethylquinoline* (L) *Complexes*.—The complexes $[Pd(dmp)L(OH_2)][ClO_4]$ (Found: C, 46.45; H, 4.7; N, 5.25. $C_{20}H_{25}ClN_2O_5Pd$ requires C, 46.6; H, 4.9; N, 5.45%) and $[Pd(dmp)L(NO_3)]$ (Found: C, 51.9; H, 5.0; N, 8.95. $C_{20}H_{23}N_3O_3Pd$ requires C, 52.25; H, 5.05; N, 9.15%) were prepared by the same methods as for the corresponding bquin and 8Me-quin complexes.[1] Hydrogen-1 n.m.r. spectra: perchlorate in $(CD_3)_2CO$, δ 3.74 (s, 2Me), 4.17 (s, 8Me), 8.51 (d, H^4, L), 2.98 (s) and 3.01 (s) (NMe_2), 4.16 (d) and 4.22 (d) (NCH_2), and 5.44 (d, H^2, dmp); nitrate in $CDCl_3$, 3.76 (s, 2Me), 4.17 (s, 8Me), 8.12 (d, H^4, L), 2.88 (s) and 2.92 (s) (NMe_2), 3.94 (d) and 4.02 (d) (NCH_2), and 5.58 (d, H^2, dmp) (selected resonances only are given).

It is to be noted that the shifts on co-ordination (p.p.m.) for the methyl groups of 2,8-dimethylquinoline in these complexes are −1.1 (2Me) and −1.4 (8Me) compared with −0.6 in 2Me-py and −1.3 in 8Me-quin in directly related complexes.[1] Particularly noticeable is the marked downfield shift of the 2Me protons in 2,8-dimethylquinoline which results from a closer approach to the metal of the 2Me group in 2,8Me$_2$-quin than in 2Me-py. This is consistent with a ligand tilt as found for [Pd(dmp)(8Me-quin)(OH$_2$)][ClO$_4$].[1]

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