Comparison of 8-Methylquinoline and Benzo[*h*]quinoline Complexes of Palladium(II) with Those of Related Ligands. Crystal and Molecular Structure of Aqua(benzo[*h*]quinoline)[2-(dimethylaminomethyl)phenyl-*N*]palladium(II) Perchlorate†

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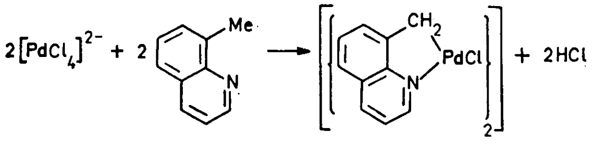
Benzo[*h*]quinoline (bquin) does not cleave the chloride bridge of [{Pd(dmp)Cl}$_2$] [dmp = 2-(dimethylaminomethyl)phenyl-*N*], 8-methylquinoline (8Me-quin) does so if in large excess, while other ligands L (pyridine, 2-methylpyridine, or 7-methylquinoline) give monomeric [Pd(dmp)Cl(L)] quantitatively. Measured equilibrium constants for the bridge-cleavage reaction indicate that the Pd $\cdots$ H–C interactions in bquin and 8Me-quin complexes are strongly destabilising. Rotations about the Pd–N bonds in [Pd(dmp)Cl(L)] are slow and no faster than equilibria involving dissociation to [{Pd(dmp)Cl}$_2$]. Stable complexes of bquin and of 8Me-quin can, however, be readily formed if the strongly bridging chloride ligands are replaced by nitrate or perchlorate. For example, stoicheiometric addition of bquin to an acetone solution derived by addition of Ag[ClO$_4$] to [{Pd(dmp)Cl}$_2$] gives the title complex, [Pd(dmp)(bquin)(OH$_2$)][ClO$_4$], the crystal and molecular structure of which has been determined by single-crystal *X*-ray diffraction. The crystals are triclinic, a = 11.050(4), b = 9.808(4), c = 11.412(5) Å, α = 77.04(4), β = 110.90(4), γ = 97.00(3)°, and Z = 2, space group $P\bar{1}$. The structure was solved by standard heavy-atom methods and refined by least squares, using 1976 observed data, to R 0.053. The co-ordination is essentially square planar with mutually *trans* nitrogen atoms. The most notable feature is the short H^{10}(bquin) $\cdots$ Pd distance [2.09(6) Å], but consistent with this being a non-bonding interaction is the *ca*. 10° tilt of the bquin (Pd–N–C 111 and 131°) in a direction that lessens this clash. From a comparison of 1,10-phenanthroline and other authentic bidentate ligands with 8Me-quin and bquin, it is concluded that the latter ligands are unidentate.

VARIOUS aromatic *N*-donor ligands (N–CH) react with [PdCl$_4$]$^{2-}$ by loss of HCl to give the complexes [{Pd(N–C)Cl}$_2$] containing a Pd–C bond, and in general this reaction requires a tertiary nitrogen and the ability to form a five-membered chelate ring.[1-3] Two ligands which undergo this reaction are interesting in that with 8-methylquinoline (8Me-quin) metallation occurs at a saturated carbon atom [equation (1)], while prior co-ordination of benzo[*h*]quinoline (bquin) through nitrogen does not allow facial interaction of the metal with the aromatic ring [equation (2)].[4] Hence neither metallation can occur as a simple electrophilic aromatic substitution.



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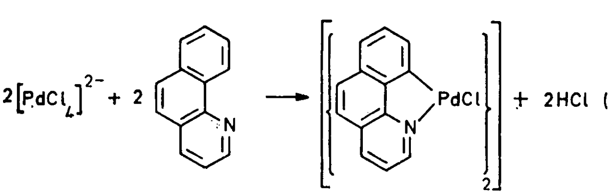

(2)

In this work we wished to establish whether normal co-ordination through nitrogen is possible for these ligands in view of the consequential close approach of hydrogen to metal atoms, to compare the stabilities of their complexes with those of pyridine or quinoline, and to see whether any structural features might be correlated with their known metallation behaviour.

RESULTS

We chose [{Pd(dmp)Cl}$_2$] [dmp = C$_6$H$_4$(CH$_2$NMe$_2$-2), a ligand derived by orthometallation of *NN*-dimethylbenzylamine] [2] as our starting material since orthopalladation of introduced ligands (bquin or 8Me-quin) is unlikely. Further, dmp provides a useful ^{1}H n.m.r. probe for structure analysis. If the co-ordination plane of the palladium is not a plane of symmetry, two singlets are expected for the CH$_3$ groups and an AB quartet for the CH$_2$ group, but two singlets only if this is a plane of symmetry. Processes leading to a plane of symmetry by time-averaging may then be studied. Two routes to bquin and 8Me-quin complexes were explored: chloride-bridge cleavage, and ligand addition after replacement of the chloride ligands by non-bridging anions.

Preparations via *Chloride-bridge Cleavage*.—Addition of pyridine(py) (2 mol per mol of complex) to [{Pd(dmp)-Cl}$_2$] gives the colourless complex [Pd(dmp)Cl(L)] (L = py),[3] and the corresponding complexes with L = 2Me-py and 7Me-quin may be prepared similarly. However, stoicheiometric addition of 8Me-quin or bquin gave no reaction as shown by the ^{1}H n.m.r. spectra of CDCl$_3$ solutions. Additions of these ligands in considerable excess enables us to detect [Pd(dmp)Cl(L)] (L = 8Me-quin) but not the bquin complex. Thus the spectrum of a solution of [{Pd(dmp)Cl}$_2$] in CDCl$_3$–8Me-quin (5 : 1 v/v) showed [Pd(dmp)Cl(L)] (L = 8Me-quin) as a minor component. Integration of signals gave an approximate value for the equilibrium constant K_3 for reaction (3) as 70 mol dm^{-3} at 30 °C.

A pure sample of [Pd(dmp)Cl(L)] (L = 8Me-quin) was

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† No reprints available.

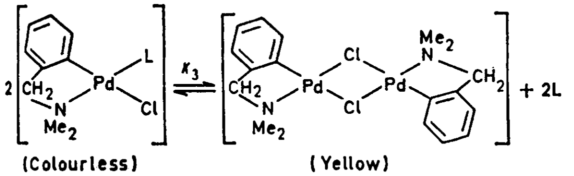
[1] A. C. Cope and R. W. Sieckman, *J. Amer. Chem. Soc.*, 1965, **87**, 3272.

[2] A. C. Cope and E. C. Friedrich, *J. Amer. Chem. Soc.*, 1968, **90**, 909.

[3] B. N. Cockburn, D. V. Howe, T. Keating, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1973, 404.

[4] G. E. Hartwell, R. V. Lawrence, and M. J. Smas, *Chem. Comm.*, 1970, 912.

isolated by dissolving the dimer in neat 8Me-quin and precipitating the product by addition of diethyl ether, but, as expected from our value of K_3, L dissociates almost completely by reaction (3) on dissolving the complex in CDCl$_3$. Values for K_3 for L = py, 2Me-py, and 7Me-quin are considerably less than the value for L = 8Me-quin and were determined spectrophotometrically in toluene (30.0 °C) by the method given in the Experimental section. There is little dependence of K_3 on L for these ligands: 4.5×10^{-5} (py), 1.3×10^{-4} (2Me-py), and 4.4×10^{-5} mol dm^{-3} (7Me-quin). Thus there is a reduction in stability of [Pd(dmp)Cl(L)] by a factor of *ca.* 10^6 with respect to equation (3) on moving the methyl group from the 7 to the 8 position in Me-quin with the following order of stability for the monomers: py $\sim$ 2Me-py $\sim$ 7Me-quin $\gg$ 8Me-quin $\gg$ bquin.



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Preparations by Use of Non-bridging Anions.—The preparation of 8Me-quin and bquin complexes by chloride-bridge cleavage is clearly unsatisfactory, but stable complexes of these ligands were synthesised by replacing chloride by non-bridging anions. Thus, after filtering off the AgCl formed by treating [{Pd(dmp)Cl}$_2$] with Ag[ClO$_4$] in acetone, addition of stoicheiometric amounts of L (8Me-quin or bquin) to the yellow solution gave the stable complexes [Pd(dmp)L(OH$_2$)][ClO$_4$]. The yellow solution probably contains [Pd(dmp)S$_2$][ClO$_4$] where S is either acetone or more likely water since the acetone was not dried. The ^{1}H n.m.r. spectrum supported this, but the diaqua-species could not be crystallised or characterised further. However, similar disolvated species have been reported to be formed from related chloride-bridged complexes.[5] The addition of an excess of L (8Me-quin or bquin) to [Pd(dmp)L(OH$_2$)][ClO$_4$] gave no reaction; [Pd(dmp)L$_2$][ClO$_4$] was not formed. This is in marked contrast to the reaction of [Pd(dmp)(OH$_2$][ClO$_4$] with py.

$$[\mathrm{Pd(dmp)(OH_2)_2}]^+ + \mathrm{L} \rightleftharpoons [\mathrm{Pd(dmp)L(OH_2)}]^+ + \mathrm{H_2O} \quad (4)$$

$$[\mathrm{Pd(dmp)L(OH_2)}]^+ + \mathrm{L} \rightleftharpoons [\mathrm{Pd(dmp)L_2}]^+ + \mathrm{H_2O} \quad (5)$$

For 8Me-quin and bquin the equilibrium constant for reaction (4) $K_4 \gg K_5$, whereas for py $K_5 \gg K_4$. Addition of 1 mol py per mol of [Pd(dmp)(OH$_2$)$_2$][ClO$_4$] gives a 1 : 1 mixture of [Pd(dmp)(OH$_2$)$_2$][ClO$_4$] and [Pd(dmp)(py)$_2$][ClO$_4$], and similarly [Pd(dmp)(py)$_2$][ClO$_4$] was the only observed product on adding py to [Pd(dmp)L(OH$_2$)][ClO$_4$] (L = 8Me-quin or bquin).

The neutral nitrato-complexes [Pd(dmp)L(NO$_3$)] (L = 8Me-quin or bquin) were prepared in a similar way to the perchlorates and show no ligand-dissociation reaction analogous to (3).

Preparation of Complexes with Bidentate Ligands.—1,10-Phenanthroline (phen) is formally related to bquin, since the former is derived by replacement of CH at the 10 position of bquin by a N atom. 1,10-Phenanthroline is, of course, a common bidentate ligand and forms [Pd(dmp)(phen)]X (X = ClO$_4$ or NO$_3$). 2,2′-Bipyridyl (bipy) similarly gives [Pd(dmp)(bipy)]X. We attempted unsuccessfully to dehydrate [Pd(dmp)(bquin)(OH$_2$)][ClO$_4$] to give [Pd(dmp)(bquin)][ClO$_4$] which might involve bidentate bquin, a direct analogue of phen. Unable to do this, we attempted to make an authentic five-co-ordinate species to compare with the pseudo-five-co-ordinate [Pd(dmp)(bquin)(NO$_3$)] (see Figure 1).

Because of the unfavourable steric interaction between *cis* ligands in square-planar complexes of 2,9-dimethyl-1,10-phenanthroline (2,9Me$_2$-phen), we were able to synthesise the five-co-ordinate complex [Pd(dmp)(2,9Me$_2$-phen)(NO$_3$)] which is stoicheiometrically equivalent to the bquin complex and exists largely in the neutral form unlike [Pd(dmp)(phen)][NO$_3$]. The molar conductance in nitrobenzene (20 °C) at 2.09×10^{-3} mol dm^{-3} is 5.60 S cm^2 mol^{-1} increasing with increased dilution, compared with *ca.* 20 S cm^2 mol^{-1} for 1 : 1 electrolytes. Similarly, the perchlorate exists as [Pd(dmp)(2,9Me$_2$-phen)(OH$_2$)][ClO$_4$] also of analogous stoicheiometry to that of the bquin perchlorate. Clearly, the lack of space for the methyl groups in the co-ordination plane has forced the 2,9Me$_2$-phen out of this plane. Rather than form an unfavourable tetrahedral geometry, a five-co-ordinate species with co-ordinated nitrate or H$_2$O is formed: an increase in co-ordination number resulting from crowding!

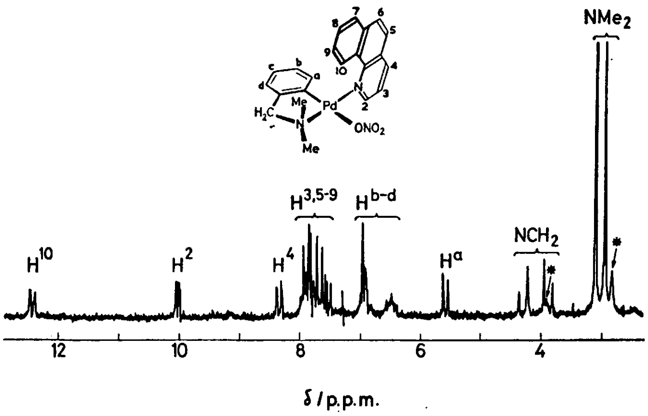
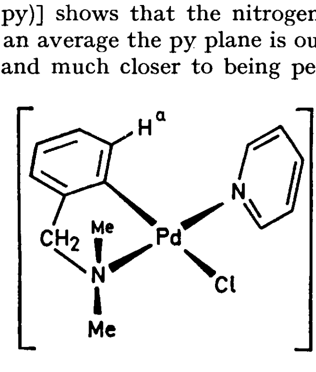


FIGURE 1 Hydrogen-1 n.m.r. spectrum of [Pd(dmp)(bquin)(NO$_3$)] recorded at 100 MHz in CDCl$_3$ at 27 °C; δ in p.p.m. downfield from SiMe$_4$ Absorptions marked with an asterisk are possibly due to [Pd(dmp)(OH$_2$)(NO$_3$)]

Structures of the Complexes.—The ^{1}H n.m.r. spectrum of [Pd(dmp)Cl(py)] shows that the nitrogen atoms are *trans* and that on an average the py plane is out of the co-ordination plane and much closer to being perpendicular to it, structure (1). We reach this conclusion from the chemical shift of H^a (δ 6.00 p.p.m.) which is significantly upfield due to



(1)

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[5] J. Dehand, M. Pfeffer, and M. Zinsius, *J. Organometallic Chem.*, 1976, **118**, C62.

the anisotropic shielding from the ring current of the adjacent py ring. The spectrum of $[Pd(dmp)Cl\{[^2H_5]py\}]$ confirmed that all the py resonances are in the range δ 7.30—8.90 p.p.m. (A similar argument has been used to assign the structures of related *N*-substituted salicylaldimine complexes.[6]) Hence, for the complexes in Table 1, $\delta(H^a) \leqslant 6.1$ p.p.m. signifies that the dmp phenyl ring is *cis* and very roughly perpendicular to the py-type ligand, while for $\delta(H^a) > 6.6$ p.p.m. no such structural relation holds. For example, for $[Pd(dmp)(py)_2][ClO_4]$ $\delta(H^a)$ is 6.04 p.p.m., but for $[Pd(dmp)(bipy)][ClO_4]$ where the aromatic rings are coplanar, $\delta(H^a) > 7.00$ p.p.m.

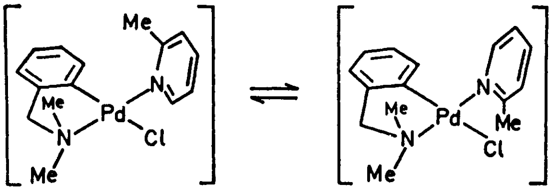
TABLE 1

Hydrogen-1 n.m.r. data [a]

Complex	dmp resonances $\delta(NCH_3)$	 $\delta(NCH_2)$	 $^2J(CH_2)$	 $\delta(H^a)$	Selected resonances of other ligands
$[\{Pd(dmp)Cl\}_2]$	2.87 (s)	3.97 (s)		*ca.* 7.1	
$[Pd(dmp)Cl(py)]$	2.97 (s)	4.00 (s)		6.00 (d)	H^2, H^6, 8.91 (m); H^3,H^5, 7.37 (m); H^4, 8.00 (m)
$[Pd(dmp)Cl(2Me\text{-}py)]$	2.96 (s) 2.98 (s)	3.89 (d) 4.05 (d)	14.7	5.77 (d)	2Me, 3.13 (s); H^6, 8.78 (m)
$[Pd(dmp)Cl(7Me\text{-}quin)]$	3.05 (s) 3.15 (s)	4.02 (d) 4.12 (d)	14.4	5.62 (d)	H^2, 9.37 (dd); H^4, 8.28 (dd); H^8, 9.17 (s); 7Me,2.58 (s)
$[Pd(dmp)Cl(8Me\text{-}quin)]$ [b]		3.59 (d) 4.03 (d)	14.2	5.73 (d)	H^2, 10.00 (dd); H^4, 8.72 (dd); 8Me 4.07 (s)
$[Pd(dmp)(OH_2)_2][ClO_4]$ [c]	2.90 (s)	4.16 (s)		>6.60	
$[Pd(dmp)(py)_2][ClO_4]$ [c]	2.88 (s)	4.25 (s)		6.04 (d)	H^2, H^6, 9.10 (dd), 9.22 (dd)
$[Pd(dmp)(bipy)][ClO_4]$ [c]	3.14 (s)	4.45 (s)		>7.00	
$[Pd(dmp)(8Me\text{-}quin)(OH_2)][ClO_4]$ [c,d]	2.93 (s) 3.01 (s)	4.04 (d) 4.38 (d)	14.0	5.69 (d)	H^2, 9.99 (dd); H^4, 8.80 (dd); 8Me, 4.06 (s)
$[Pd(dmp)(bquin)(OH_2)][ClO_4]$ [c,d]	2.97 (s) 3.17 (s)	4.09 (d) 4.47 (d)	14.6	5.98 (d)	H^2 9.96 (dd); H^4, 8.78 (dd); H^{10}, 12.64 (m)
$[Pd(dmp)(2.9Me_2\text{-}phen)(OH_2)][ClO_4]$ [c]	3.17 (s)	4.30 (s)		5.20 (d)	2,9Me_2, 3.38 (s); H^3, H^8, 7.98 (d); H^4, H^7, 8.65 (d); H^5, H^6, 8.12 (s)
$[Pd(dmp)(phen)][NO_3]$ [e]	3.31 (s)	4.25 (s)		>6.80 (d)	H^2, H^9, 9.32 (dd), 9.23 (dd); H^4, H^7, 8.03 (dd), 8.75 (dd); H^3, H^8, 8.23 (dd), 8.05 (dd); H^5, H^6, 8.16 (s)
$[Pd(dmp)(8Me\text{-}quin)(NO_3)]$	2.89 (s) 2.91 (s)	3.86 (d) 4.22 (d)	13.9	5.61 (d)	H^2, 10.01 (dd); H^4, 8.30 (dd); 8Me, 4.02 (s)
$[Pd(dmp)(bquin)(NO_3)]$	2.94 (s) 3.10 (s)	3.93 (d) 4.31 (d)	13.9	5.58 (d)	H^2, 10.02 (dd); H^4, 8.32 (dd); H^{10}, 12.42 (m)
$[Pd(dmp)(2,9Me_2\text{-}phen)(NO_3)]$	3.07 (s)	4.10 (s)		5.41 (d)	2,9Me_2, 3.49 (s); H^3, H^8, 7.56 (dd); H^4, H^7, 8.12 (d); H^5, H^6, 7.64 (s)

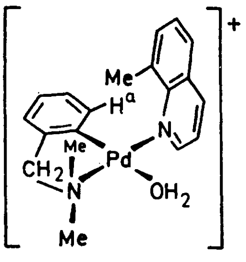
[a] Recorded in $CDCl_3$, unless stated otherwise, at 27 °C and 100 MHz; δ in p.p.m. relative to $SiMe_4$. [b] Recorded in $CDCl_3$–8Me-quin (5 : 1 v/v); NMe signals obliterated by those of free 8Me-quin. [c] Recorded in $(CD_3)_2CO$. [d] Measured at −20 °C. [e] Measured at −60 °C; at 27 °C pairs of phen signals coalesced to three dd at δ 9.36 (*J* 5.5 and 1.3), 8.82 (*J* 8.2 and 1.3), and 8.18 p.p.m. (*J* 5.5 and 8.2 Hz). Added phen gives separate signals at 27 °C and so is not involved in the exchange.

For $[Pd(dmp)Cl(2Me\text{-}py)]$ the lack of rapid rotation at 27 °C as in process (6) is established by the observation in the ^1H n.m.r. spectrum of two singlets and an AB quartet for the CH_2 and CH_3 groups of dmp. The temperature variation of the spectrum (27—120 °C in $[^2H_8]$toluene), showing a broadening and shifting of absorptions at higher temperatures, is inconsistent with process (6) alone since we observed a considerable change in the average chemical shift which should not occur. We interpret these spectral changes as resulting from changes in rate and in the position of equilibrium (3). The equilibrium is sufficiently rapid at higher temperatures to mask any observation of process (6). A toluene solution of $[Pd(dmp)Cl(2Me\text{-}py)]$ becomes reversibly more yellow on heating and at 120 °C the ^1H n.m.r. spectrum is best interpreted as that of a mixture of $[\{Pd(dmp)Cl\}_2]$ and 2Me-py.



(6)

The ^1H n.m.r. spectra of $[Pd(dmp)L(OH_2)][ClO_4]$ (L = 8Me-quin and bquin) are consistent with structures (2) and (3), in particular $\delta(H^a)$ is 5.69 and 5.98 p.p.m. respectively for these complexes. Co-ordinated water was identified by ν(OH) at 3 400 cm^{-1} and a two-proton n.m.r. absorption of variable shift (δ 3—4 p.p.m.). Unco-ordinated perchlorate was identified by a very strong absorption at 1 080 cm^{-1}. The lack of a plane of symmetry through palladium is apparent in the ^1H n.m.r. spectra of both complexes at −20 °C, but coalescence of the non-equivalent NMe signals at room temperature is due to a process discussed in the following paper. Co-ordination shifts for the bquin and 8Me-quin ligands are considered in the Discussion section.



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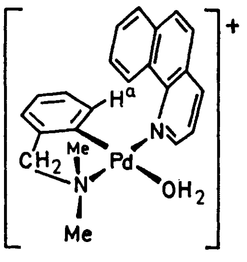

(3)

A single-crystal *X*-ray diffraction study has shown that

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[6] R. E. Reichert and B. O. West, *J. Organometallic Chem.*, 1973, **54**, 391.

the molecular structure (where L = bquin) which we deduced to be present in solution is also found in the crystal.

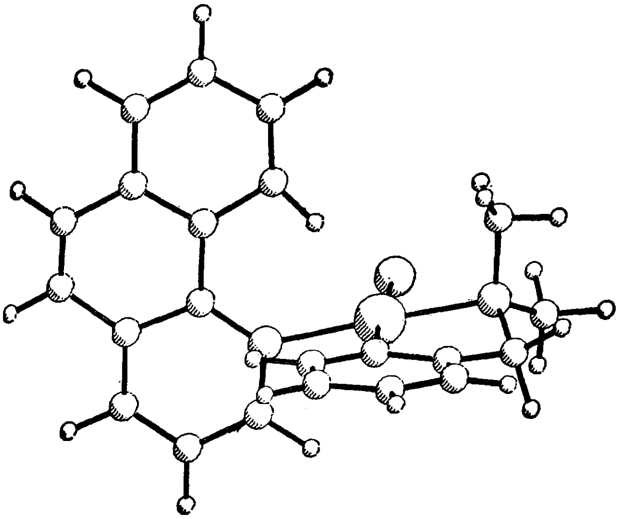

FIGURE 2 General view of the cation $[Pd(dmp)(bquin)(OH_2)]^+$

The structure found is shown in Figure 2, whilst in Figure 3 interatomic distances and bond angles relating to the co-ordination of the (bquin) ligand and its actual geometry are given. The remaining bond lengths and angles are given in Figure 4, and the unit-cell contents are shown in Figure 5. From Figure 3, the effect of the Pd · · · H clash in the bquin co-ordination can be clearly seen. The hydrogen atom makes a very close approach to the metal of *ca.* 2.09 Å, but even so the ligand is tilted away from a symmetrical co-ordination (*i.e.* equal Pd–N–C angles) by *ca.* 10°. It is interesting to note that the Pd · · · H contact is very similar to Mo · · · H–C distances (1.93 and 2.15 Å) found in two molybdenum diethyldipyrazolylborato-complexes in which the interaction is considered to be bonding, with the two electrons in the C–H bond incorporated into a three-centre Mo–H–C system to produce an 18-electron configuration for the Mo atoms.[7] It is estimated that the Mo–H bond strengths may be as much as 71—84 kJ mol^{-1}. In the case of our palladium complex the stability of the 16-electron square-planar configuration leads one to adopt the view that here the interaction is of the non-bonding type.

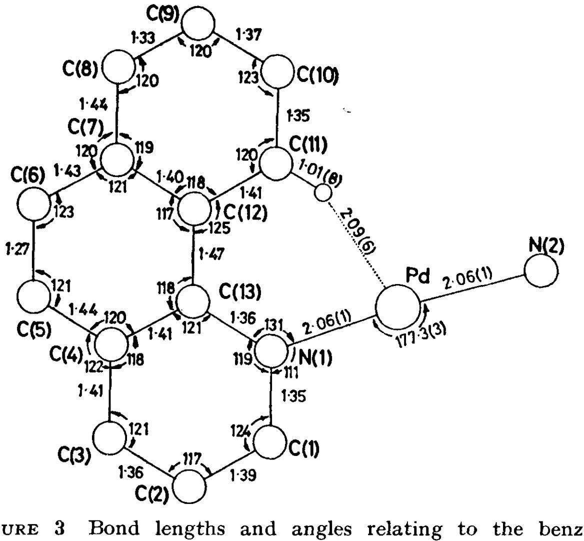

FIGURE 3 Bond lengths and angles relating to the benzoquinoline ligand and its tilted co-ordination to the Pd atom. Estimated standard deviations in C–C and C–N distances are 0.02 Å and in C–C–C, C–C–N, and C–N–C angles are 1°

The nitrato-complexes $[Pd(dmp)L(NO_3)]$ (L = 8Me-quin and bquin) are structurally comparable with (2) and (3) but with co-ordinated nitrate (absorptions at 1 020, 1 290, and 1 430 cm^{-1}) having replaced co-ordinated water. Figure 1 shows the ^1H n.m.r. spectrum of $[Pd(dmp)(bquin)(NO_3)]$ which is very similar to that of $[Pd(dmp)(bquin)(OH_2)][ClO_4]$ except for the lack of the H_2O signal, and shows separate NMe singlets. Different NMe groups are also indicated by the ^{13}C n.m.r. spectrum of the corresponding 8Me-quin complex (signals 51.27 and 52.17 p.p.m. downfield from $SiMe_4$, in $CDCl_3$ solution).

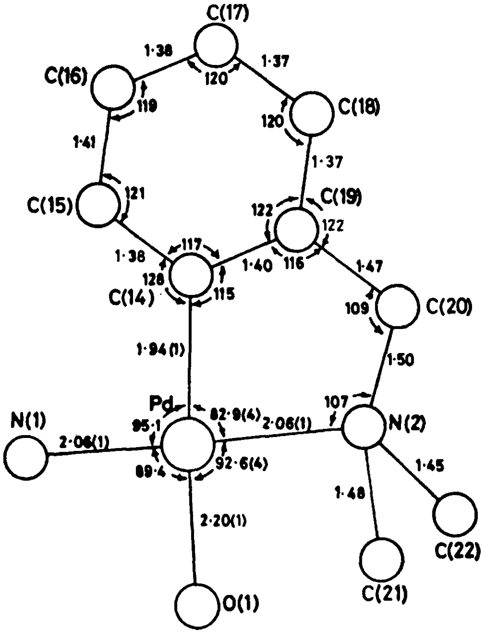

FIGURE 4 Bond lengths and angles relating to the Pd co-ordination and the geometry of the 2-(dimethylaminomethyl)-phenyl ligand. Estimated standard deviations involving light-atom parameters are as given for Figure 3

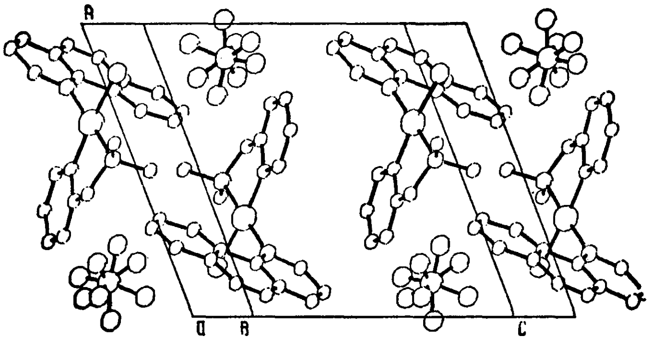

FIGURE 5 View of the unit-cell contents for $[Pd(dmp)(bquin)(OH_2)][ClO_4]$

In contrast to these nitrato-complexes, $[Pd(dmp)(phen)][NO_3]$ is ionic so that with the bidentate ligand phen a

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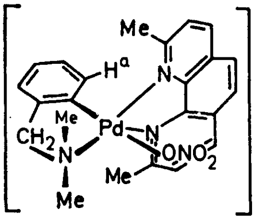
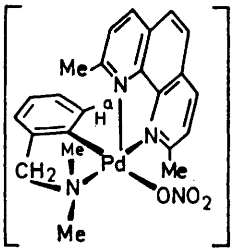
[7] F. A. Cotton and A. G. Stanislowsky, *J. Amer. Chem. Soc.*, 1974, **96**, 5074; F. A. Cotton and V. W. Day, *J.C.S. Chem. Comm.*, 1974, 415.

normal square-planar complex is obtained, whereas the related bquin ligand is clearly unidentate. The ^1H n.m.r. spectrum of [Pd(dmp)(phen)][NO_3] in $CDCl_3$ is temperature dependent. At −60 °C two sets of resonances for H^2, H^3, and H^4 and for H^7, H^8, and H^9 of the phen ligand were observed indicating non-equivalent nitrogen atoms as expected, but at room temperature the coalescence of appropriate pairs of signals indicated a rapid interchange of the phen nitrogen atoms between the two co-ordination sites. The stoicheiometrically equivalent 2,9Me_2-phen complex is essentially non-conducting in concentrated solutions and we believe it forms a neutral five-co-ordinate species which is bright yellow-orange in contrast to the colourless phen cation. However, it does show a small, but strongly concentration-dependent, conductance in dilute nitrobenzene solutions. This indicates an electrolyte–non-electrolyte equilibrium with nitrate dissociation suppressed at higher concentrations. This is possibly reaction (7). In $CDCl_3$ at concentrations where the non-electrolyte would predominate the ^1H n.m.r. spectrum shows that a single species is present, which gives only two Me singlets and a singlet for the CH_2 group, implying a plane of symmetry through the dmp and equivalent N atoms in 2,9Me_2-phen. Furthermore, the high-field doublet for H^a imposes structural restrictions as discussed earlier. Only the trigonal-bipyramidal structure (4) fits these conditions, but we believe that there is a dynamic structure of lower symmetry containing no plane of symmetry and non-equivalent methyl groups in 2,9Me_2-phen. There is selective signal broadening below −50 °C; the CH_2 and NMe_2 signals broaden first on cooling, the 2,9Me_2-phen signals later, but this does not necessarily mean that different processes are occurring. Even at the lowest temperature we could obtain (−93 °C), sharp limiting spectra were not observed. Hence, both the structure and solution behaviour of [Pd(dmp)(2,9Me_2-phen)(NO_3)] are uncertain. The rapid process occurring might be (7), but alternatively the molecule might have the square-pyramidal structure (5), analogous to the bquin complex but in this case an authentic five-co-ordinate species, with a rapid oscillation of the 2,9Me_2-phen ligand from one side of the co-ordination plane to the other.

$$[Pd(dmp)(2,9Me_2\text{-phen})(NO_3)] \rightleftharpoons [Pd(dmp)(2,9Me_2\text{-phen})][NO_3] \quad (7)$$



(4)



(5)

DISCUSSION

The conditions under which M · · · H–C interactions are stabilising or destabilising are not clear. The molybdenum molecules described above [7] appear to be the only established cases of bonding interactions and it seems that, with square-planar d^8 complexes, hydrogen atoms of ligands are frequenctly located directly above or below the co-ordination plane, to fill otherwise unoccupied space, reducing repulsions elsewhere, rather than because of a bonding interaction. The tilt of the ligand bquin in [Pd(dmp)(bquin)(OH_2)][ClO_4] and the equilibrium constants for reaction (3) support this view for palladium(II) complexes. In particular, the considerable stability of the 7Me-quin compared with the 8Me-quin complex clearly indicates that enforced interaction of type Pd · · · H–C leads to destabilisation. With the extremely rigid bquin ligand the Pd · · · H distance may only be increased at the expense of Pd–N bonding. While the relative stabilities of bquin and 8Me-quin complexes with respect to reaction (3) cannot be uniquely ascribed, it appears that destabilisation results largely from angular deformation rather than Pd–N bond lengthening.

The close approach of hydrogen to palladium atoms leads to the most striking feature of the ^1H n.m.r. spectra of the 8Me-quin and bquin complexes. This is the large downfield shift on co-ordination of the ^1H signal of the 8Me group of 8Me-quin and H^{10} of bquin. There is a similar downfield co-ordination shift for the 8Me group in the ^{13}C n.m.r. spectrum of [Pd(dmp)-(8Me-quin)(NO_3)] in $CDCl_3$ solution from 18.10 to 22.10 p.p.m. relative to $SiMe_4$. The downfield shifts for nuclei in regions close to the vacant fifth and sixth co-ordination sites of square-planar d^8 complexes are due to paramagnetic anisotropy of the metal atom [8,9] and increase with decreasing Pd–H distance, reaching a maximum when the Pd–H vector is perpendicular to the co-ordination plane. As a consequence of the downfield shift of H^{10} of bquin and the upfield shift of H^a of dmp, there is a remarkable 6.88 p.p.m. spread of aromatic signals for [Pd(dmp)(bquin)(NO_3)] as shown in Figure 1. Some average co-ordination shifts are given in Figure 6 for some ligands we have examined. The chemical shifts (δ) for H^{10} are 12.4 and 12.6 p.p.m. for [Pd(dmp)-(bquin)(NO_3)] and [Pd(dmp)(bquin)(OH_2)][ClO_4] respectively, compared with δ 9.3 for the free ligand, an average co-ordination shift of −3.2 p.p.m. The co-ordination shift is only −1.3 p.p.m. for the 8Me group of 8Me-quin so that, although these hydrogens can approach the metal atom as closely as H^{10} of bquin, each spends about one third of its time this close to the metal so that the co-ordination shifts are correspondingly smaller. Moreover, if the rapid rotation about the CH_3–C bond in co-ordinated 8Me-quin could be slowed down, possibly by compression of the Me group against the metal atom, separate signals with a considerable chemical shift between them are to be expected. However, the 8Me singlet for [Pd(dmp)(8Me-quin)(NO_3)] is only slightly broadened in $CHFCl_2$ at −130 °C so that the rotation barrier must be small.

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EXPERIMENTAL

Preparation of Complexes.—The parent complex di-μ-chloro-bis{[2-(dimethylaminomethyl)phenyl-*N*]palladium(II)}, [{Pd(dmp)Cl}$_2$], was prepared as described by Cope and Friedrich.[2] Analytical and conductance data for the new complexes are given in Table 2.

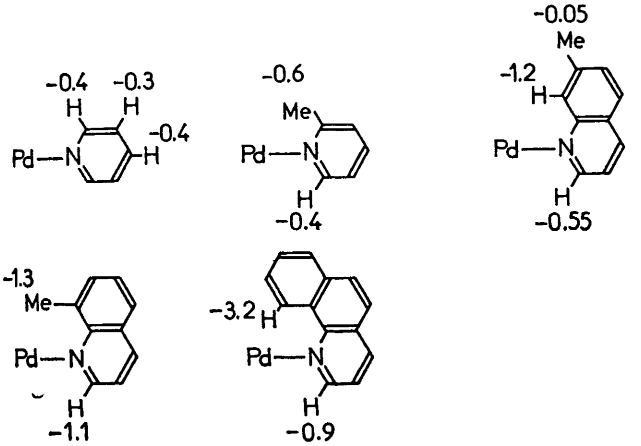

FIGURE 6 Hydrogen-1 n.m.r. shifts (p.p.m.) on co-ordination to Pd^{II} for complexes in Table 1

TABLE 2

Analytical [a] and conductance data

Complex	Analysis (%) C	H	N	Cl	Λ [b]/S cm^2 mol^{-1}
[Pd(dmp)Cl(py)]	47.15 (47.35)	4.80 (4.80)	7.75 (7.90)	10.3 (10.0)	
[Pd(dmp)Cl(2Me-py)]	48.5 (48.8)	5.20 (5.20)	7.55 (7.60)	10.3 (9.60)	
[Pd(dmp)Cl(7Me-quin)]	54.25 (54.45)	5.20 (5.05)	6.65 (6.70)	8.80 (8.45)	
[Pd(dmp)Cl(8Me-quin)]	54.45 (54.45)	5.20 (5.05)	6.60 (6.70)	9.15 (8.45)	
[Pd(dmp)(py)$_2$][ClO$_4$]	45.65 (45.8)	4.50 (4.45)	8.40 (8.45)		24.5 (1.56 × 10^{-3})
[Pd(dmp)(bipy)][ClO$_4$]	45.8 (46.0)	4.10 (4.05)	8.25 (8.45)		25.5 (0.91 × 10^{-3})
[Pd(dmp)(8Me-quin)(OH$_2$)][ClO$_4$]	45.35 (45.55)	4.60 (4.65)	5.65 (5.60)		19.5 (1.98 × 10^{-3})
[Pd(dmp)(bquin)(OH$_2$)][ClO$_4$]	48.9 (49.15)	4.30 (4.30)	5.25 (5.20)		19.0 (1.30 × 10^{-3})
[Pd(dmp)(2,9Me$_2$-phen)(OH$_2$)][ClO$_4$]	48.55 (48.8)	4.60 (4.60)	7.30 (7.40)		21.0 (1.80 × 10^{-3})
[Pd(dmp)(phen)][NO$_3$]	50.95 (52.24)	4.10 (4.20)	11.2 (11.6) [c]		22.8 (3.08 × 10^{-3})
[Pd(dmp)(bquin)(NO$_3$)]	54.6 (54.8)	4.50 (4.40)	8.60 (8.75)		
[Pd(dmp)(8Me-quin)(NO$_3$)]	50.85 (51.2)	4.70 (4.75)	9.75 (9.45)		
[Pd(dmp)(2,9Me$_2$-phen)(NO$_3$)]	53.7 (54.1)	4.80 (4.75)	10.6 (10.95)		*d*

[a] Calculated values are given in parentheses. [b] Measured in nitrobenzene at 20 °C; concentrations (mol dm^{-3}) are given in parentheses. [c] O, 9.9 (9.25%). [d] Λ/S cm^2 mol^{-1} (concentration/mol dm^{-3}): 4.41 (4.26 × 10^{-3}), 5.60 (2.09 × 10^{-3}), and 9.22 (0.63 × 10^{-3}).

Chloride-bridge-splitting reactions. These were carried out simply by addition of stoicheiometric amounts of py, 2Me-py, or 7Me-quin to yellow solutions of [{Pd(dmp)Cl}$_2$] in chloroform to give almost colourless solutions which yielded [Pd(dmp)Cl(py)], [Pd(dmp)Cl(2Me-py)], or [Pd(dmp)Cl(7Me-quin)] respectively as colourless crystals in good yield from chloroform–diethyl ether mixtures. The 8Me-quin complex is not formed in this way. Pyridine as a minor impurity in commercial 8Me-quin reacts preferentially and so was removed by recrystallisation of the 8Me-quin complex with zinc chloride, followed by neutralisation and ether extraction or simply by distillation, rejecting fractions below 245 °C. Purified 8Me-quin (1.2 cm^3) was added to [{Pd(dmp)Cl}$_2$] (0.10 g) to give a suspension which cleared to give a pale yellow solution. Addition of diethyl ether gave the product *[Pd(dmp)Cl(8Me-quin)]* as a flocculent colourless precipitate which was washed with diethyl ether and dried in air (0.15 g, 96%). Attempts to recrystallise gave [{Pd(dmp)Cl}$_2$]. No evidence was found for a similar chloride-bridge cleavage by bquin.

Perchlorate salts. A solution containing [Pd(dmp)(solvent)$_2$][ClO$_4$] was prepared by adding a stoicheiometric amount of silver perchlorate to a suspension of [{Pd(dmp)Cl}$_2$] in acetone. Silver chloride, precipitated while the solution was agitated for 5 min, was removed by filtration and the appropriate ligand was added to this yellow solution. Pyridine (4 mol per mol of dimer), bipy, 8Me-quin, bquin, or 2,9Me$_2$-phen (each 2 mol per mol of dimer) were added and addition of diethyl ether and recrystallisation of the precipitate from acetone–light petroleum mixtures gave [Pd(dmp)(py)$_2$][ClO$_4$] (colourless, 64%), [Pd(dmp)(bipy)][ClO$_4$] (colourless, 52%), [Pd(dmp)L(OH$_2$)][ClO$_4$][L = 8Me-quin (pale yellow, 61%), bquin (pale yellow, 56%), or 2,9Me-phen (bright orange-yellow, 63%)] as good quality crystals.

Nitrato-complexes. By preparations similar to those above, but using silver nitrate in aqueous methanol or acetone, followed by recrystallation from chloroform–diethyl ether mixtures, the following complexes were prepared: [Pd(dmp)(NO$_3$)L][L = 8Me-quin (colourless, 40%), bquin (colourless, 43%), or 2,9Me$_2$-phen (yellow-orange, 79%)] and [Pd(dmp)(phen)][NO$_3$] (colourless, 99%).

Determination of the Equilibrium Constants for Reaction (3).—Solutions of the complexes [Pd(dmp)Cl(L)] in toluene were accurately prepared using weighed amounts of carefully recrystallised complex, and absoption measurements at 343.5 (L = py or 2Me-py) or 370.0 nm (L = 7Me-quin) gave the extent of dissociation to [{Pd(dmp)Cl}$_2$] since only the palladium complexes (the dimer more strongly) absorb in that region. Isosbestic points observed on making incremental additions of L support the presence of only two palladium species in solution. Molar absorption coefficients for monomers were determined in the presence of a large excess of L: 610 ± 20 (L = py), 570 ± 20 (2Me-py), and 2 530 ± 30 dm^3 mol^{-1} cm^{-1} (dimer) at 343.5 nm and 260 ± 15 (L = 7Me-quin) and 1 440 ± 25 dm^3 mol^{-1} cm^{-1} (dimer) at 370.0 nm. From equation (3) we deduce $K = (a - x)^3/2x^2$ where x is the measured concentration of [Pd(dmp)Cl(L)] and a its concentration assuming no dissociation. This expression holds experimentally since K calculated in this way is independent of a.

X-Ray Structure Analysis of [Pd(dmp)(bquin)(OH$_2$)][ClO$_4$].—Crystals were obtained as variously shaped yellow blocks from acetone–light petroleum. Most were crazed and were unsuitable for single-crystal work, but eventually one irregularly shaped fragment was found which gave

TABLE 3

Atomic fractional co-ordinates ($\times 10^4$)

Atom	x	y	z
Pd(1)	3 376(1)	1 345(1)	2 513(1)
Cl(1)	1 174(3)	0 975(3)	−2 369(3)
O(2)	1 366(18)	0 006(19)	−3 026(17)
O(3)	−0 129(19)	1 254(21)	−2 791(18)
O(4)	1 856(23)	0 327(23)	−1 124(21)
O(5)	0 689(24)	2 306(23)	−3 076(20)
O(6)	0 692(24)	0 524(24)	−1 302(23)
O(7)	1 827(26)	2 161(25)	−2 723(24)
O(8)	2 446(26)	1 440(29)	−1 726(27)
O(9)	0 637(39)	−0 111(46)	−3 111(39)
N(1)	2 164(7)	2 748(9)	2 574(7)
C(2)	0 846(11)	2 954(17)	3 810(12)
H(2)	0 455(11)	2 502(17)	4 562(12)
C(3)	0 528(11)	4 253(18)	3 105(13)
H(3)	−0 111	4 848	3 305
C(4)	1 020(9)	4 851(13)	2 115(11)
C(5)	0 723(12)	6 248(16)	1 379(17)
H(5)	0 128	6 873	1 606
C(6)	1 152(13)	6 753(15)	0 466(16)
H(6)	0 895	7 798	−0 064
C(7)	1 952(10)	5 995(13)	0 120(12)
C(8)	2 366(13)	6 599(14)	−0 950(13)
H(8)	2 128	7 658	−1 448
C(9)	3 029(13)	5 853(18)	−1 341(13)
H(9)	3 351	6 325	−2 136
C(10)	3 335(13)	4 512(17)	−0 708(12)
H(10)	3 845	3 920	−1 063
C(11)	2 981(12)	3 884(14)	0 313(11)
H(11)	3 284(122)	3 032(80)	1 003(94)
C(12)	2 290(9)	4 628(11)	0 772(9)
C(13)	1 839(8)	4 047(11)	1 860(9)
C(14)	4 962(9)	2 227(11)	3 517(8)
C(15)	5 142(11)	3 549(12)	3 793(10)
H(15)	4 319	4 199	3 472
C(16)	6 376(13)	4 072(14)	4 476(12)
H(16)	6 495	5 102	4 704
C(17)	7 429(12)	3 245(17)	4 859(11)
H(17)	8 389	3 634	5 365
C(18)	7 271(10)	1 925(14)	4 589(9)
H(18)	8 091	1 275	4 887
C(19)	6 056(9)	1 424(11)	3 942(8)
C(20)	5 817(9)	−0 016(10)	3 702(8)
H(201)	6 645	−0 337	3 556
H(202)	5 652	−0 715	4 513
N(2)	4 635(7)	−0 058(9)	2 541(7)
C(21)	5 009(12)	0 444(16)	1 390(9)
H(211)	4 219(47)	0 557(70)	0 592(50)
H(212)	5 650(53)	1 246(50)	1 277(118)
H(213)	5 415(57)	−0 455(43)	1 470(69)
C(22)	4 141(13)	−1 497(15)	2 564(14)
H(221)	3 442(50)	−1 403(94)	1 697(32)
H(222)	3 713(65)	−1 798(89)	3 233(52)
H(223)	4 715(57)	−2 265(56)	2 651(58)
O(1)	1 681(9)	0 262(14)	1 317(11)

Hydrogen atoms are numbered according to the carbon atom to which they are attached.

satisfactory X-ray photographs and this was used for all the subsequent X-ray work.

Crystal data. $C_{22}H_{23}ClN_2O_5Pd$, $M = 501.60$, Triclinic, $a = 11.050(4)$, $b = 9.808(4)$, $c = 11.412(5)$ Å, $\alpha = 77.04(4)$, $\beta = 110.90(4)$, $\gamma = 97.00(3)°$, $U = 1\ 124.8$ Å^3, $D_m = 1.46$, $Z = 2$, $D_c = 1.48$ g cm^{-3}, $F(000) = 544$, space group $P\bar{1}$, Mo-K_α radiation, $\lambda = 0.710\ 69$ Å, μ(Mo-K_α) 31.2 cm^{-1}.

Intensity data were recorded from the crystal fragment mounted in an arbitrary orientation on a Nonius CAD4 diffractometer. Procedures used for the determination of accurate cell dimensions and orientations and data collection (ω—2θ scans) were as previously described,[10] with, in this case, parameters for the scan given by width $= 1.0 \pm 0.3\tan\theta$ and $1.5 < \theta < 23°$. One hemisphere of data was recorded ($\pm h$, $\pm k$, $+l$) and the total 3 258 intensities measured reduced to 3 132 on merging equivalent reflections (R 0.008). Of these, 1 976 satisfied the condition $I > 2\sigma(I)$,[10] and were used in the subsequent structure analysis and refinement. The structure was solved using Patterson and electron-density syntheses and refined by blocked full-matrix least squares using the SHELX program.[11]

During the latter stages of refinement problems occurred with the hydrogen atoms and the oxygen atoms of the perchlorate group. Whilst most hydrogen-atom positions could be determined from difference syntheses, it was found to be more convenient to use the AFIX and DFIX facilities in SHELX. Thus H atoms on the aromatic rings were fixed on the bisectors of the relevant C_β–C_α–C_β angles at a C–H distance of 0.98 Å, whilst those on the methyl groups were fixed at a C–H distance of 1.08 Å with an H $\cdots$ H distance of 1.76 Å. One exception to this was H(11) which makes a close approach to the metal atom: this was allowed to refine freely, and fortunately seems fairly well defined ($U_{iso.}$ 0.18 Å^2). The ClO_4 group was treated as two interlocking tetrahedra with a common centre (the chlorine atom) and with the eight oxygen atoms assigned occupancies of 0.5. Whilst the final refinement and difference synthesis indicate that this simple model is not really adequate, we feel that the quality of the data does not merit a more detailed treatment. At the end of refinement R 0.053 4 and R' 0.054 1, with the weighting scheme $w = 1/[\sigma^2(F) + 0.000\ 7F^2]$ giving the best agreement analyses. The final co-ordinates are listed in Table 3; thermal parameters, lists of observed and calculated structure factors, and analyses of agreement have been deposited as Supplementary Publication No. 22322 (16 pp.).* Atomic scattering factors for Pd, Cl, C, N, and O were taken from ref. 12 and for H from ref. 13.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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