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η^3-Allyl Complexes of Palladium Containing 7,8-Benzoquinoline and 8-Methylquinoline

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Displacement of the chloride ligands from $[Pd(\eta^3\text{-}all)Cl]_2$ *(all = allyl, 2-methylallyl or 1,3-dimethylallyl) by treatment with* $AgNO_3$ *or* $AgClO_4$ *gives acetone-soluble species. These were not isolated but were reacted with 7,8-benzoquinoline (bquin) or 8-methylquinoline (8-Mequin) to give complexes of type* $[Pd(all)L_2]ClO_4$ *(L = bquin or 8-Mequin),* $[Pd(all)XL]$ *(X =* NO_3*, L = bquin or 8-Mequin; X =* ClO_4*, L = 8-Mequin) or* $[Pd(all)(H_2O)(8\text{-}Mequin)]ClO_4$*. Thus there is nothing preventing coordination of two ligands such as bquin or 8-Mequin, one largely above the other below the coordination plane. From DNMR observations on* $[Pd(all)(bquin)_2]ClO_4$*, exchange of the ends of the* η^3*-allyl has the same rate as exchange of the bquin ligands. The fastest dynamic process for* $[Pd(all)(H_2O)(8\text{-}Mequin)]ClO_4$ *involves* H_2O *dissociation with the 8-Mequin passing from being largely on one to largely on the other side of*

TABLE I. Analytical and Conductometric Data.

Compound		Analyses[a]				Λ_M (Concentration)[b]
		C	H	N	Cl	
$[Pd(C_3H_5)(bquin)_2]ClO_4$	(*1a*)	57.05	4.00	4.6	6.0	16.5 (2.55×10^{-3})
		(57.35)	(4.15)	(4.6)	(5.85)	20.3 (1.28×10^{-3})
$[Pd(C_4H_7)(bquin)_2]ClO_4$	(*1b*)	58.35	4.65	4.05	5.35	15.7 (3.41×10^{-3})
		(58.0)	(4.4)	(4.5)	(5.7)	20.1 (1.71×10^{-3})
$[Pd(C_5H_9)(bquin)_2]ClO_4$	(*1c*)	57.55	4.30	4.20	6.45	16.3 (2.88×10^{-3})
		(58.6)	(4.60)	(4.40)	(5.60)	20.1 (1.44×10^{-3})
$[Pd(C_3H_5)(8\text{-}Mequin)_2]ClO_4$	(*2*)	48.1[c]	4.3	4.75	6.8	16.8 (3.34×10^{-3})
		(51.8)	(4.35)	(5.25)	(6.65)	19.3 (1.67×10^{-3})
$[Pd(C_3H_5)(NO_3)(bquin)]$	(*3a*)	49.45	3.8	7.15		
		(49.3)	(3.9)	(7.2)		
$[Pd(C_4H_7)(NO_3)(bquin)]$	(*3b*)	50.25	4.05	6.75		
		(50.55)	(4.25)	(6.95)		
$[Pd(C_5H_9)(NO_3)(bquin)]$	(*3c*)	55.54[d]	4.47	6.51		
		(51.75)	(4.58)	(6.70)		
$[Pd(C_3H_5)(NO_3)(8\text{-}Mequin)]$	(*4a*)	44.1	4.05	8.25		
		(44.25)	(4.0)	(7.95)		
$[Pd(C_4H_7)(NO_3)(8\text{-}Mequin)]$	(*4b*)	46.05	4.5	7.35		
		(45.85)	(4.4)	(7.65)		
$[Pd(C_4H_7)(ClO_4)(8\text{-}Mequin)]$	(*5*)	41.85	4.05	3.45	8.8	12.8 (4.40×10^{-3})
		(41.6)	(4.0)	(3.45)	(8.75)	15.3 (2.20×10^{-3})
$[Pd(C_3H_5)(H_2O)(8\text{-}Mequin)]ClO_4$	(*6a*)	38.7	3.55	3.75	8.65	12.2 (4.19×10^{-3})
		(38.45)	(3.45)	(3.45)	(8.75)	15.0 (2.09×10^{-3})
$[Pd(C_4H_7)(H_2O)(8\text{-}Mequin)]BF_4$	(*6b*)	40.85	4.4	3.4		18.0 (4.29×10^{-3})
		(41.05)	(4.45)	(3.4)		20.8 (2.15×10^{-3})

[a] Found % with calculated figures in parentheses. [b] Molar conductances/Ω^{-1} cm^2 mol were measured in nitrobenzene at 15 °C at the concentrations/mol dm^{-3} given in parentheses. [c] Cannot be recrystallised to improve purity. [d] Too little material available to achieve analytical purity. ^1H n.m.r. spectra support the formulation.

the coordination plane while retaining its coordination position trans *to one end of the η^3-allyl group.*

Introduction

The 7,8-benzoquinoline ligand (bquin) in crystals of $[Pd(o\text{-}C_6H_4CH_2NMe_2)(H_2O)(bquin)]ClO_4$ is as shown in Figure 1 with a very close approach (2.09 Å) of the 10-H to the palladium atom [1]. This distance would be significantly less if the bquin were not tilted by about 10° (CNPd angles 111° and 131°) so as to reduce this repulsive H–Pd interaction. This complex was prepared by addition of bquin to $[Pd(o\text{-}C_6H_4CH_2NMe_2)(H_2O)_2]ClO_4$, itself prepared from the chloro-bridged dimer $[Pd(o\text{-}C_6H_4CH_2NMe_2)Cl]_2$. Even with an excess of bquin the second H_2O is not substituted to give the bis(bquin) complex. In contrast pyridine gives $[Pd(o\text{-}C_6H_4CH_2NMe_2)(py)_2]ClO_4$ directly. Yet there appear to be no particular reasons preventing coordination of two bquin ligands, one largely above, one below the coordination plane, so we turned our attention to the smaller more flexible chelate ligands, η^3-allyls, to work out a chemistry similar to that above and to see whether two bquin ligands could coordinate. This proved so, and our results are described here.

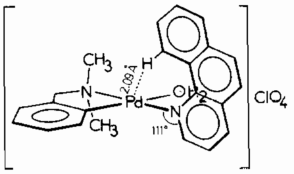
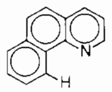


Figure 1. Structure of $[Pd(o\text{-}C_6H_4CH_2NMe_2)(H_2O)(bquin)]ClO_4$.

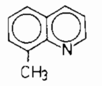
Results and Discussion

Preparation of Compounds

Compounds (*1*) to (*6*) (Table I) were prepared as in the Scheme. Treatment of a suspension of $[Pd(\eta^3\text{-all})Cl]_2$ (all = allyl, 2-methylallyl or 1,3-dimethylallyl) in undried acetone with $AgClO_4$ followed by addition of bquin to the yellow solution so formed gave $[Pd(\eta^3\text{-all})(bquin)_2]ClO_4$ (*1*) with no evidence for formation of $[Pd(\eta^3\text{-all})(H_2O)(bquin)]ClO_4$ even when one mol of ligand is added (see scheme). After



bquin



8-Mequin

Preparative Scheme
*Presumed intermediates

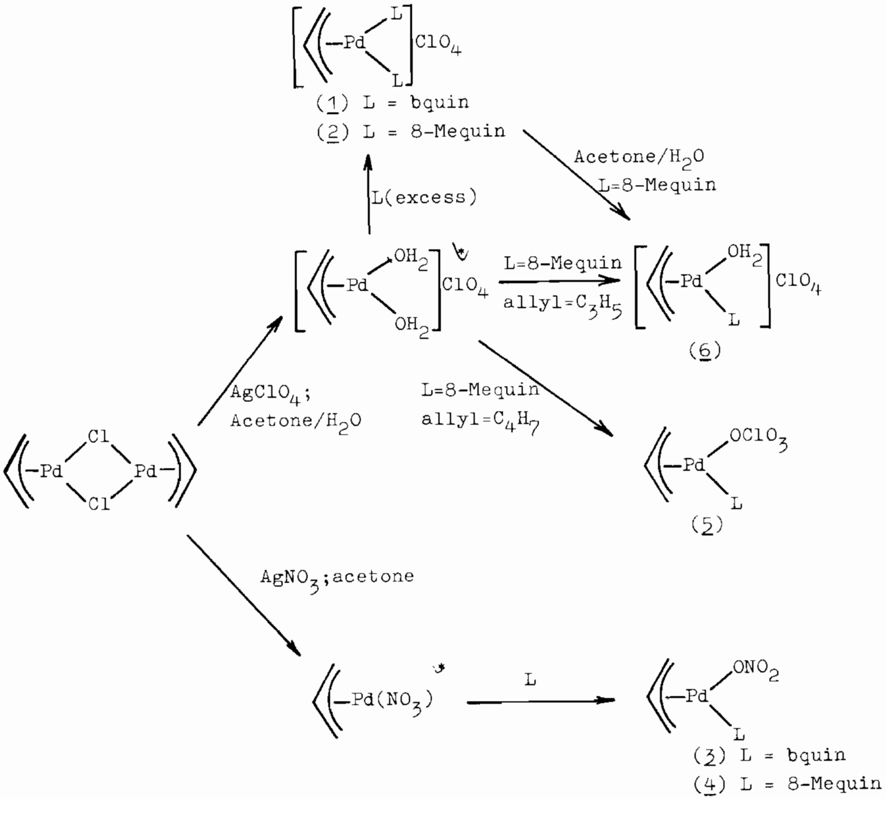
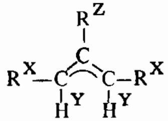


TABLE II. Selected ^{1}H N.m.r. Data (100 MHz) for Ligands and New Compounds as Recorded at "frozen-out" Temperatures.

Compound		Solvent and Temperature/°C	Chemical Shifts (δ) for 8-Mequin or bquin			Chemical Shifts (δ) for η^3-allyl Group		
			2-H	10-H	8-CH$_3$	H^X or Me^X	H^Y	H^Z or Me^Z
bquin		CDCl$_3$ (27)	8.96dd	9.30m				
8-Mequin		CDCl$_3$ (27)	8.91dd		2.81s			
[Pd(C$_3$H$_5$)(bquin)$_2$]ClO$_4$		CD$_2$Cl$_2$ (−50)	9.14dd	10.17m		5.00d	4.24d	6.68m
(*1a*)			8.82dd	9.76m		4.80d	4.06d	
[Pd(C$_4$H$_7$)(bquin)$_2$]ClO$_4$		CD$_2$Cl$_2$ (−60)	8.59d	9.58d		4.48s	3.79s	2.14s
(*1b*)			8.15d	9.23d		4.32s	3.56s	
[Pd(C$_5$H$_9$)(bquin)$_2$]ClO$_4$		CDCl$_3$ (−50)	8.74d	9.92d		c		
(*1c*)			8.18d	9.48d				
[Pd(C$_3$H$_5$)(8-Mequin)$_2$]ClO$_4$		CD$_2$Cl$_2$ (−70)	8.88d		3.09s	c		
(*2*)			9.31d		3.40s			
[Pd(C$_3$H$_5$)(NO$_3$)(bquin)]	Isom (A)	CDCl$_3$ (−65)	9.08dd	11.02m		4.41(br), 3.20(br)	3.50d, 2.62d	5.60m
(*3a*)	Isom (B)		9.66dd	10.58m			3.42d, 2.50d	
[Pd(C$_4$H$_7$)(NO$_3$)(bquin)]	Isom (A)	CDCl$_3$ (−60)	9.07d	11.02d		4.18s, 3.00s	3.28s, 2.51s	2.17s
(*3b*)	Isom (B)		9.65d	10.78m			2.38s	
[Pd(C$_5$H$_9$)(NO$_3$)(bquin)]	Isom (A)	CDCl$_3$ (−50)	9.13(br)	10.98(br)		1.38(br)^d	4.04(br)	5.23m
(*3c*)	Isom((B)		9.68(br)	10.67(br)				
[Pd(C$_3$H$_5$)(NO$_3$)(8-Mequin)]	Isom (A)	CDCl$_3$ (−60)	9.24dd		3.72s	4.31(br), 3.78(br)	3.40(br), 2.84(br)	5.74(br)
(*4a*)	Isom (B)		9.79dd		3.30s			
[Pd(C$_4$H$_7$)(NO$_3$)(8-Mequin)]	Isom (A)	CDCl$_3$ (−50)	9.21d		3.70s	4.08s, 3.68(sh)	3.31(sh), 2.80s	2.34s
(*4b*)	Isom (B)		9.75d		3.34s	3.54s	3.10s, 2.68s	2.24s
[Pd(C$_4$H$_7$)(ClO$_4$)(8-Mequin)]^e		CD$_2$Cl$_2$ (−90)	9.34(br)		3.49s	4.32, 3.82s	3.33s, 2.90s	2.30s
(*5*)								
[Pd(C$_3$H$_5$)(H$_2$O)(8-Mequin)]ClO$_4$		CD$_3$COCD$_3$ (+20)	9.54dd		3.50s	4.50d	3.42d	6.08m
(*6a*)		(−40)	9.64(br)		3.64s	4.36d, 4.19^d	3.52d, 3.33d	6.12m
	Isom (A)	(−80)	9.43d		3.78s	4.35(br), 4.20(br)	3.54(br), 3.37(br)	6.15(br)
	Isom (B)	(−80)	9.98d		3.35s			

[a] Other resonances of 8-Mequin and bquin occur in the range δ7.0 to 8.3. With the exception of the 4-H signal they are either not resolved or assigned. [b] The η^3-allyl is labelled:



(R = H or Me). [c] Allyl signals either not recorded or assigned clearly. [d] At 20 °C the averaged Me^X doublet is at δ0.71; at −50 °C one Me signal is at δ1.38, the other estimated to be at δ0.04, too close to the lock signal to record. [e] Either there is only one isomer or isomer-interchange is not frozen-out even at −90 °C. In acetone a very different spectrum is probably due mainly to [Pd(C$_4$H$_7$)(solv)(8-Mequin)]ClO$_4$, two isomers of which are obtained at low temperatures.

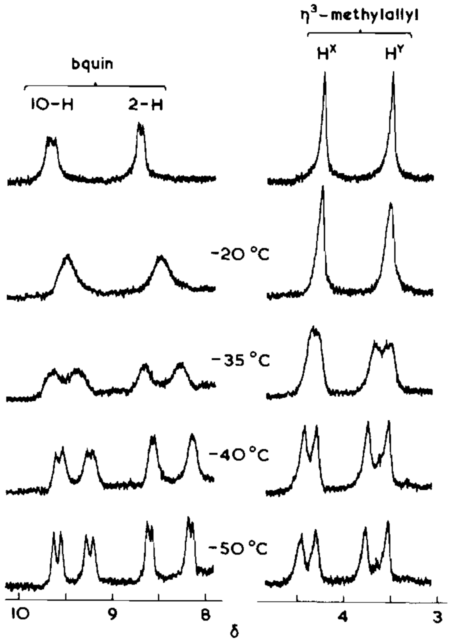


Figure 2. ^1H n.m.r. spectra (selected signals) for $[Pd(\eta^3-C_4H_7)(bquin)_2]ClO_4$ (*1b*) in CD_2Cl_2.

a similar treatment with 8-methylquinoline (8-Mequin) in large excess, crystals of $[Pd(\eta^3\text{-all})(8\text{-Mequin})_2]ClO_4$ (*2*) were obtained which persist in CD_2Cl_2 solution but readily give $[Pd(\eta^3\text{-all})(H_2O)(8\text{-Mequin})]ClO_4$ (*6*) with moist acetone in the absence of an excess of 8-Mequin. The bis(bquin) complex is more readily formed and more stable than the bis(8-Mequin) complex, and for example it dissolves unchanged in both CD_2Cl_2 and CD_3COCD_3 in the absence of an excess of bquin. Complex (*6*) is a solid product formed where all = allyl(C_3H_5) but not where all = 2-methylallyl (C_4H_7). For a reason we do not understand the ClO_4^- ion coordinates in the latter case, displacing H_2O, to give complex (*5*) (see scheme). The perchlorate ion is coordinated in the crystal (1140, 1104, 1020 and 894 cm^{-1}) and in CD_2Cl_2 solutions. However, a very different ^1H n.m.r. spectrum is found in acetone to that in CD_2Cl_2 and nitrobenzene solutions are conducting; we believe that palladium-solvated 1:1 electrolytes are formed in these solvents. The coordinating abilities of the anions decrease in the order $NO_3^- > ClO_4^- > BF_4^-$ and by use of $AgBF_4$ we were able to synthesise $[Pd(C_4H_7)(H_2O)(8\text{-Mequin})]BF_4$ (*6b*) since water can successfully compete with BF_4^- for the coordination site in this case. Nitrato-complexes (*3*) and (*4*) corresponding to the perchlorato-complex (*5*) are readily prepared as in the scheme and exist as neutral species in $CDCl_3$ solution.

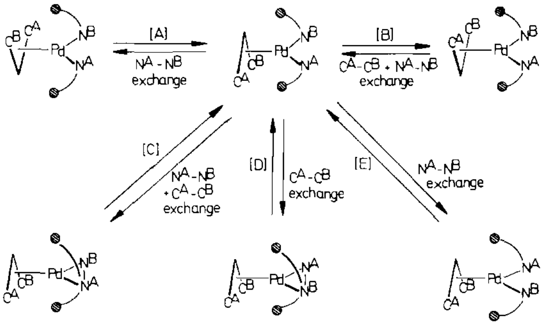


Figure 3. Possible interconversions of $[Pd(\eta^3\text{-all})(bquin)_2]ClO_4$ (*1*) leading to $C^A–C^B$ and/or $N^A–N^B$ exchange. Of these only (B) and (C) give both $C^A–C^B$ and $N^A–N^B$ exchange. ⊗ denotes the 10-H of bquin.

The most significant structural feature of these complexes is the necessary close approach of certain hydrogen atoms (10-*H* for bquin and 8-C*H*$_3$ for 8-Mequin) to the metal and this was expected to give downfield coordination shifts for these protons in the ^1H n.m.r. spectra [1, 2, 3]. Generally this is so (Table II). The 8-C*H*$_3$ signal (δ2.81 for free ligand) is at δ3.09 to 3.78 in the 8-Mequin complexes. An even wider range (δ9.23 to 11.02) is found for the 10-*H* signal of coordinated bquin with even a small upfield coordination shift in one case. In $[Pd(C_6H_4CH_2NMe_2)(H_2O)(bquin)]ClO_4$ the bquin plane and the coordination plane are closely perpendicular [1] and the downfield coordination shift is 3.34 p.p.m. whereas for the allyl complexes the maximum observed shift is 1.72 p.p.m. Intrinsically smaller shifts might occur in the allyl systems for electronic reasons but we believe that the major cause of variation of shift within the series (*1*) to (*6*) is the angular variation between the coordination and ligand planes. As the ligand is rotated from being perpendicular to being in the coordination plane, coordination shifts should change from downfield to upfield. For the 10-*H*(bquin) signal, an average downfield coordination of 0.39 p.p.m., where two bquin are coordinated, should be compared with 1.54 p.p.m. when only one is coordinated. It is probable that interaction between the two bquin ligands prevents the adoption of conformations as closely perpendicular as when only one bquin is coordinated.

Dynamic Behaviour of Complexes (1)

All the complexes in Tables I and II are dynamic with ^1H n.m.r. coalescences in the range −60° to 27 °C, but in all cases the *syn* and *anti* signals of the η^3-allyls are clearly resolved at the higher temperature (no *syn–anti* exchange) so we can rule out η^3–η^1 interconversions at room temperature and below for all the compounds described. Compounds (*1*) give spectra at 27 °C consistent with a symmetrical allyl and equivalent bquin ligands whereas molecules with the expected structure (as those in Figure 3) are chiral with non-equivalent bquin ligands and non-equivalent ends to the η^3-allyl. Lowering the tempera-

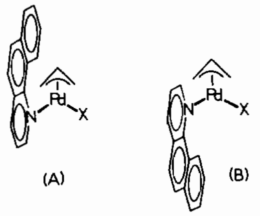


Figure 4. Geometric isomers (A) and (B) for compounds (*3*); the 8-Mequin (*4*) and (*6*) show similar isomerism.

ture to –60 °C results in spectra (for example, Figure 2) consistent with the structures as expected. All the complexes (*1a–c*) show similar temperature dependence of n.m.r. spectra. The four pairs of signals of the 2-methylallyl complex illustrated in Figure 2 all coalesce in a pair-wise manner with coalescence temperatures in the range –35 °C to –20 °C just as expected if these exchanges all result from the same process. Thus the non-equivalent bquin ligands exchange at the same rate as the asymmetric η^3-allyl becomes symmetric by time-averaging. Of the five possible exchanges illustrated in Figure 3, two involve movement of the η^3-allyl and three require the combined movement of both bquin ligands. Only exchanges (B) and (C) lead to C^A–C^B and N^A–N^B exchange at the same rate but we have no evidence to distinguish these or either from a totally random exchange. (B) is an allyl-flip (the plane of the allyl passing into the coordination plane and out on the other side, without *syn–anti* exchange), and although the allyl-flips have been suggested (with and without *syn–anti* exchange) the evidence for such is slight and it is certainly not a typical low-energy process for η^3-allyls of palladium [4]. A dissociative mechanism seems most likely for (C), every loss of bquin requiring the remaining bquin to rotate into and through the coordination plane with a free bquin returning to the same coordination site from which one was lost. We favour this mechanism by analogy with the behaviour of [Pd(all)(H_2O)(8-Mequin)] ClO_4 but have no evidence for it here, except that the addition of bquin to solutions of (*1*) at 27 °C does lead to rapid exchange of free with coordinated bquin. Complex (*1*) must be too crowded to allow an associative exchange so we favour this dissociative pathway.

The complex [Pd(η^3-C_3H_5)(8-Mequin)$_2$] ClO_4 (*2*) in CD_2Cl_2 shows a single set of 8-Mequin resonances at 20 °C which resolves into two equal intensity sets at –70 °C as expected for behaviour analogous to that of (*1*). Compound (*2*) however, in CD_3COCD_3 shows a single set of ligand resonances at 20 °C, but analysis of the frozen-out n.m.r. spectrum (–75 °C) shows that (*2*) is only a minor component of a mixture also containing free 8-Mequin and a species we believe is [Pd(η^3-C_3H_5)(8-Mequin)(solvent)] ClO_4, which exists as two isomers of the type discussed below.

TABLE III. Mol Fractions (±0.05) of Isomers (A) and (B) (Figure 4) Measured from "Frozen-out" ^{1}H N.m.r. Spectra at the Temperatures Given.

Compound	Solvent	Temp./°C	Isomer (A)	Isomer (B)
(*3a*)	$CDCl_3$	–65	0.55	0.45
(*3b*)	$CDCl_3$	–60	0.25	0.75
(*3c*)	$CDCl_3$	–55	0.70	0.30
(*4a*)	$CDCl_3$	–60	0.50	0.50
(*4b*)	$CDCl_3$	–50	0.53	0.47
(*6a*)	CD_3COCD_3	–80	0.30	0.70

Isomerism and Dynamic Behaviour of Compounds (3) to (6)

These complexes all give ^{1}H n.m.r. spectra at around –50 to –80 °C consistent with frozen-out structures. Two geometric isomers as in Figure 4 are found for each; the mol fractions (Table III) were obtained by integration of spectra at the temperatures given. For the compounds (*3a*), (*3b*) and (*3c*) there is a distinct variation in the populations of these isomers depending only on the nature of the η^3-allyl. It is not straightforward to assign the geometric isomers in Figure 4 to the appropriate sets of n.m.r. signals for the two isomers (Table I). However, we have made assignments by assuming that substitution at the η^3-allyl in the 2-position by a Me-group would destabilise the isomer with the bulk of the bquin on that side of the coordination plane. With one such assignment, the rest follow automatically since chemical shifts are quite characteristic of the isomers.

The nitrato-complexes (*3*) and (*4*) undergo *syn–syn, anti–anti* allyl exchange at the same rate (within experimental error) as the rate of exchange of isomers (A) and (B) but no comment on the mechanism is justified. The aquo-complexes (*6a*) are different in that exchange between the ends of the η^3-allyl (*syn–syn, anti–anti* exchange) is slower than the interconversion of isomers (A) and (B). Figure 5 shows that at 20 °C the η^3-allyl appears symmetrical and there is only one set of 8-Mequin signals. On cooling the *syn* and *anti* signals broaden first and by –40 °C these have resolved into four separate doublets (T_c ~ –20 °C) while the only slight broadening of the 2-*H* signal is observed at this temperature. By –40 °C site exchange between H_2O and 8-Mequin is slow on an n.m.r. time-scale. Between –40 °C and –80 °C the *Me*-signal and the 2-*H* signals of the 8-Mequin broaden and separate into two sets of signals for isomers (A) and (B) respectively (T_c ~ –70 °C). Thus movement of the 8-Mequin from above to below the coordination plane is considerably faster than coordination site-exchange between the H_2O and 8-Mequin ligands as shown in Figure 6. Similar observations were made on [Pd(η^3-crotyl)Cl(2-methylpyridine)] where a simple rotation about

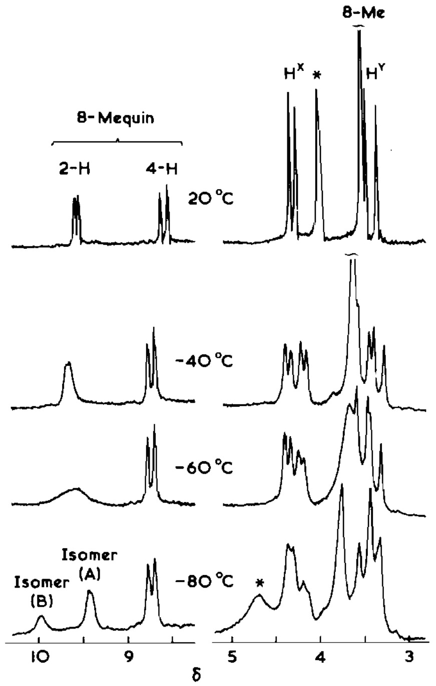


Figure 5. ^{1}H n.m.r. spectra for [Pd(C_3H_5)(H_2O)(8-Mequin)] ClO_4 (*6a*); only the 2-*H* and 4-*H* signals of 8-Mequin and the group of signals at highest shift (*syn* and *anti* hydrogens H^X and H^Y, and *Me*) are shown. Absorption (*) due to H_2O moves downfield with reducing temperature and finally resolves into two, one component of which is shown in the −80 °C spectrum.

the Pd–NC_6H_7 bond is possible [5]. We believe that rotation of the 8-Mequin past a *cis*-ligand (as for the 2-Mepy) is prohibited and suggest that as the rotation occurs the H_2O ligand is displaced only to return when the ligand has passed by the *cis*-coordination site. Retention of configuration at the metal is thus maintained in this fast process. This mechanism is directly analogous to that we have proposed for the dynamic behaviour of [Pd(o-$C_6H_4CH_2NMe_2$)(H_2O)L] ClO_4 (L = 8-Mequin or bquin) [6].

Conclusion

One or two of the ligands 8-Mequin or bquin may be coordinated to palladium(II) leading to crowded molecules and which totally block one or two sites above or below the square coordination plane. Dynamic behaviour is unlikely to occur intramolecularly or by associative processes, so dissociative mechanisms are prefered.

Experimental

Preparation of Compounds

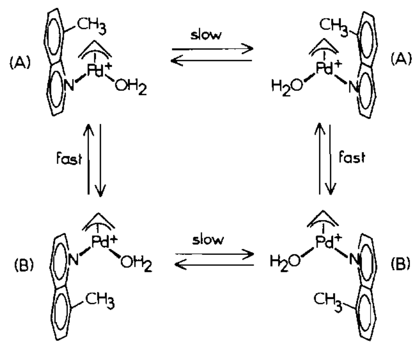


Figure 6. Proposed mechanistic scheme for [Pd(C_3H_5)(H_2O)(8-Mequin)]ClO_4 (*6a*).

The complexes [Pd(η^3-all)Cl]$_2$, where all = allyl (C_3H_5), 2-methylallyl (C_4H_7) or 1,3-dimethylallyl (C_5H_9), were prepared by reported methods [7]. The new compounds were all prepared by treatment of a suspension of [Pd(η^3-all)Cl]$_2$ in acetone with the calculated amount of $AgNO_3$, $AgClO_4$ or $AgBF_4$ (in the one case) in acetone to precipitate all the chloride. After a short time all the palladium complex had dissolved and the AgCl was filtered off. Acetone solutions of 7,8-benzoquinoline or 8-methylquinoline (2 or 4 mol per mol Pd dimer) were added to the pale yellow solution to give crystals of the product on standing or on addition of diethylether. The perchlorates were recrystallised from CH_2Cl_2 solutions by adding ether, and the nitrates from $CHCl_3$ on adding ether. The compounds in Table II were prepared in this way, except (*2*) which required an excess of 8-Mequin in solution to be formed. Recrystallisation of (*2*) from acetone, precipitating with ether, gave (*6a*). Yields appear to be essentially quantitative, except that yields after recrystallisation are in the range 50–90%.

Spectroscopic Studies

^{1}H n.m.r. spectra were recorded on a Varian HA100 spectrometer with temperature calibration from chemical shifts for neat MeOH.

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