# Co-ordination Chemistry of 8-Methyl-, 8-Ethyl-, and 8-Isopropyl-quinoline-2-carboxaldehyde-N-methylimine with Palladium, Rhodium, and Iridium. Crystal and Molecular Structure of (η-Allyl)(8-isopropyl-quinoline-2-carboxaldehyde-N-methylimine-NN′)palladium(II) Perchlorate

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

Michael B. Hursthouse and **K. M. Abdul Malik**, Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS

The co-ordination chemistry of the new potentially bidentate ligands 8-methyl-, 8-ethyl-, and 8-isopropyl-quinoline-2-carboxaldehyde-N-methylimine (mqa, eqa, and iqa respectively), $8-RC_9H_5N-CH=NMe$, with palladium, rhodium, and iridium is reported. Hydrogen-1 and ^{13}C n.m.r. spectra are used to show that there is unidentate co-ordination through the CH=NMe nitrogen atom in the complexes $[RhCl(C_8H_{12})(mqa)]$, $[Pd(O_2CMe)_2(mqa)_2]$, and $[PdCl(C_6H_4CH_2NMe_2-2)(mqa)]$ with the 3-H of the quinolyl group positioned above the co-ordination plane. Bidentate co-ordination is found in the complexes $[RhCl(CO)_2L]$ and $[Pd(η-allyl)L]X$ (allyl = allyl or 2-methylallyl; X = ClO_4 or BF_4; L = mqa, eqa, or iqa). The crystal and molecular structure of $[Pd(η-C_3H_5)(iqa)][ClO_4]$ has been determined by X-ray methods. Crystals are monoclinic, $a = 8.598(1)$, $b = 8.142(1)$, $c = 27.400(3)$ Å, $\beta = 97.151(1)°$, space group $P2_1/c$, and $Z = 4$. The structure has been solved by the heavy-atom method and refined by full-matrix least squares to $R = 0.041$ for 2 437 diffractometer data. The η-allyl group is essentially normal but slightly asymmetric in a way consistent with the CH=NMe having a greater *trans* influence than the quinoline group. The major feature is the relief of an unacceptably close approach of the Pr^i group to the Pd atom, resulting largely from the metal atom being 1.09 Å out of the C_5N plane of the quinoline ligand. Carbon–hydrogen cleavage (oxidative addition) at the 3-position of the quinolyl group leads to the hydrido-complexes $[MH(Cl)(mqa - H^3)\{P(C_6H_{11})_3\}_2]$ (M = Rh or Ir), whereas palladation leads to metallation at different positions. The particular site of palladation may be controlled by the other ligands and it is argued that uni- and bi-dentate co-ordination lead to palladation at the 3-position and at the 8-Me group respectively. The sites of metallation have been determined from ^1H and ^{13}C n.m.r. spectra of soluble derivatives.

WE have synthesised a series of 8-substituted quinoline-2-carboxaldehyde-N-methylimines as potentially bidentate ligands related to the unidentate ligands 8-methylquinoline (8Me-quin) and 7,8-benzoquinoline

qa (R = H)
mqa (R = Me)
eqa (R = Et)
iqa (R = Pr^i)
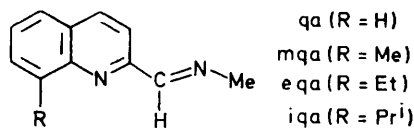
(benzo[h]quinoline, bquin). Previously we have shown that in palladium(II) complexes of 8Me-quin and bquin the ligand planes lie approximately perpendicular to the co-ordination planes so that the hydrogen atoms forced


8Me-quin   bquin
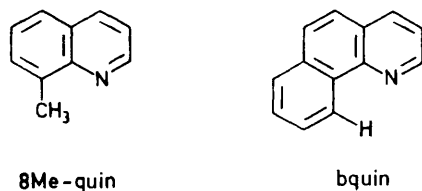
close to the metal (8-CH_3 and 10-H) occupy ' axial ' sites above the co-ordination plane with destabilising Pd · · · H interactions.[1] If the ligands mqa, eqa, and iqa could be made to adopt bidentate co-ordination through both nitrogen atoms, we expected the group R to lie in the co-ordination plane in a site *trans* to the co-ordinated imine nitrogen, with the possibility of unusual H–Pd interactions and/or enforced low co-ordination numbers

for the metal. In exploring the co-ordination of these ligands we have synthesised complexes (1)—(34) (Table 1), mainly of palladium(II), and by correlating ^1H and ^{13}C n.m.r. data we have shown that four distinct bonding modes occur, two of which result from C–H cleavage. Bidentate co-ordination in square-planar d^8 complexes was deduced spectroscopically and subsequently confirmed by a single-crystal X-ray diffraction study of $[Pd(η-C_3H_5)(iqa)][ClO_4]$. Some aspects of reactions leading to the metallated products have already been communicated.[2]

RESULTS AND DISCUSSION

The ligands qa, mqa, eqa, and iqa were synthesised as indicated in Scheme 1 by essentially standard procedures. Complexes of these ligands (Table 1, Scheme 2, and Experimental section) gave good quality crystals in most cases which were sufficiently soluble for ^1H and ^{13}C n.m.r. analysis except for $[PdCl_2(qa)]$ (7), $[PdCl_2(mqa)]$ (11), $[PdCl_2(mqa)_2]$ (8), $[PdCl(mqa - H^8)]$ (25), $[\{PdCl(mqa - H^3)\}_2]$ (28) and eqa and iqa analogues of (8) and (28). Soluble derivatives of the isomers (25) and (28) were prepared to enable the sites of metallation (8-Me or 3-H) to be determined by means of n.m.r. spectroscopy. The most convenient derivatives for this purpose were $[PdCl(mqa - H^8)(PEt_3)]$ (26) and $[PdCl(mqa - H^3)(NC_5D_5)]$ (32) (NC_5D_5 = $[^2H_5]$pyridine) and the corresponding NC_5D_5 complexes (33) (eqa) and (34) (iqa). From ^1H (Table 2) and ^{13}C (Table 3) n.m.r. data it was possible to establish that bonding types (I)—(IV) occur
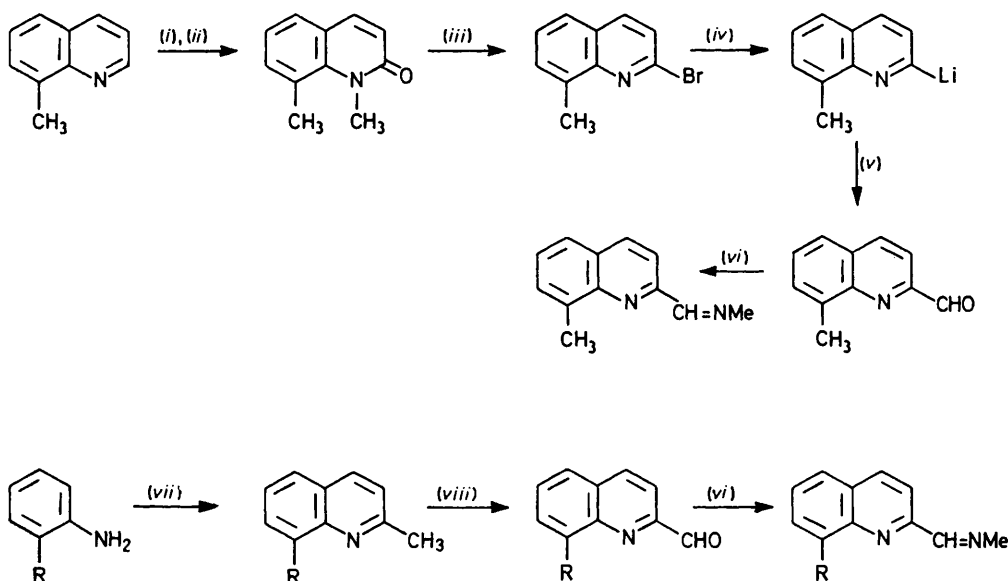
Scheme 1 Synthesis of ligands: (*i*) Me_2SO_4; (*ii*) K[OH], $[Fe(CN)_6]^{2-}$, water; (*iii*) PBr_5; (*iv*) LiBu, OEt_2; (*v*) dimethylformamide (dmf); (*vi*) $NMeH_2$, EtOH; (*vii*) $(CH_3CHO)_n$, HCl; (*viii*) SeO_2, dioxan, water

in complexes (1)—(34). The metallated ligands as in (III) and (IV) are symbolised as given.

Compounds with Unidentate Co-ordination (I).—Unidentate co-ordination was observed for the soluble

complexes $[Pd(O_2CMe)_2(mqa)_2]$ (12), [PdCl(dmp)(mqa)] (13) (dmp is the bidentate ligand 2-NN-dimethylamino-methylphenyl, $C_6H_4CH_2NMe_2$; see ref. 1), and [RhCl-(cod)(mqa)] (4) (cod = cyclo-octa-1,5-diene) prepared by
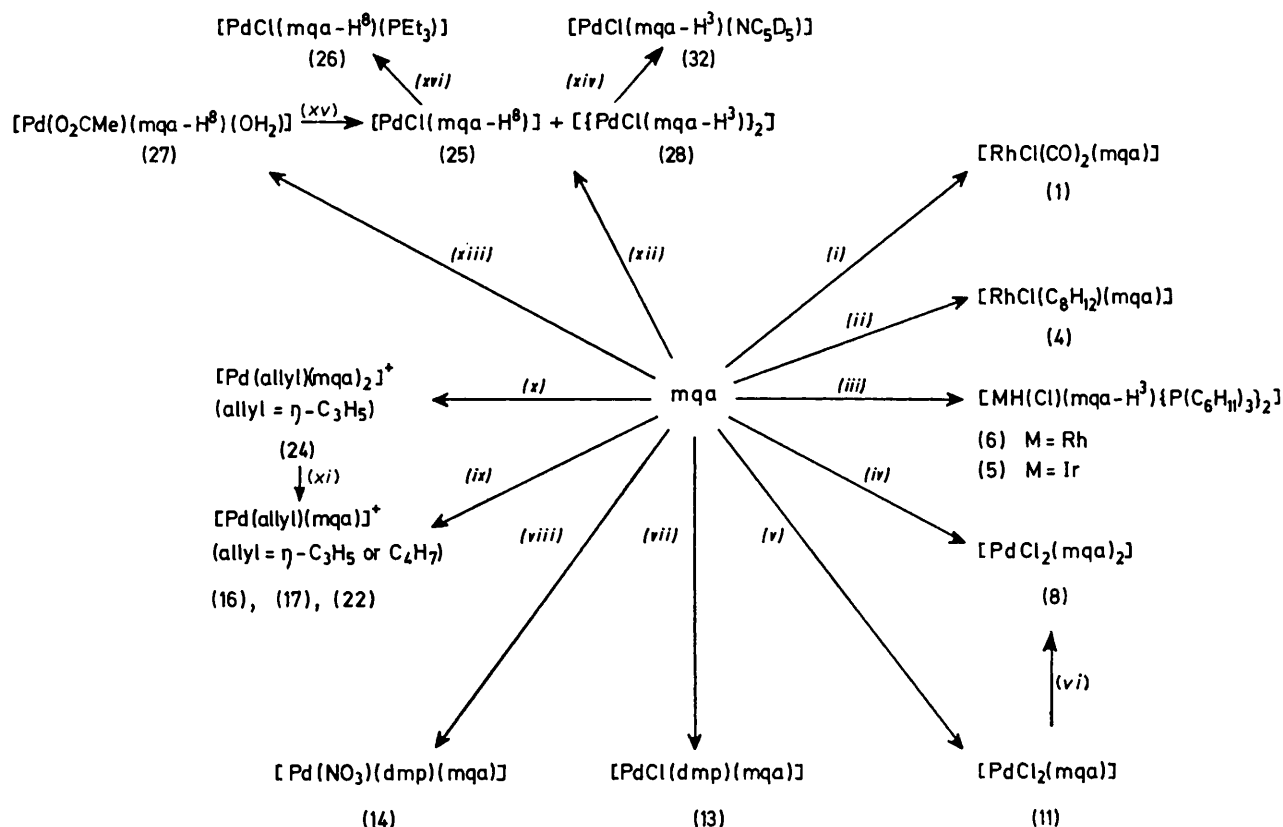
Scheme 2 Synthesis of complexes: (*i*) $[\{RhCl(CO)_2\}_2]$; (*ii*) $[\{RhCl(C_8H_{12})\}_2]$; (*iii*) $[\{MCl(C_8H_{14})_2\}_2]$-$P(C_6H_{11})_3$; (*iv*) $[PdCl_4]^{2-}$, 20 °C; (*v*) $[PdCl_2(NCPh)_2]$; (*vi*) mqa; (*vii*) $[\{PdCl(dmp)\}_2]$; (*viii*) $[\{PdCl(dmp)\}_2]$-Ag[NO_3]; (*ix*) $[\{PdCl(allyl)\}_2]$-Ag[ClO_4] or -Ag[BF_4]; (*x*) As (*ix*) with excess of mqa; (*xi*) $CDCl_3$; (*xii*) $[PdCl_4]^{2-}$, reflux in MeOH; (*xiii*) $[\{Pd(O_2CMe)_2\}_3]$-CHCl_3; (*xiv*) NC_5D_5; (*xv*) Cl⁻; (*xvi*) PEt_3

TABLE 1

Analytical [a] and conductance data

Analysis (%)

Compound	C	H	N	Cl	P	Λ [b]/Ω^{-1} cm² mol⁻¹
Non-metallated						
(1) [RhCl(CO)$_2$(mqa)]	44.6 (44.4)	3.2 (3.2)	7.5 (7.4)	9.4 (9.35)		
(2) [RhCl(CO)$_2$(eqa)]	46.0 (45.9)	3.7 (3.6)	7.15 (7.15)	8.9 (9.05)		
(3) [RhCl(CO)$_2$(iqa)]	47.3 (47.25)	4.0 (3.95)	6.85 (6.9)	8.6 (8.7)		
(4) [RhCl(COD)(mqa)]	55.65 (55.75)	5.55 (5.6)	6.4 (6.5)	8.5 (8.25)		
Metallated						
(5) [IrH(Cl)(mqa − H³){P(C₆H₁₁)₃}₂]	59.1 (59.25)	8.35 (8.1)	2.5 (2.9)	3.45 (3.65)	6.2 (6.35)	
(6) [RhH(Cl)(mqa − H³){P(C₆H₁₁)₃}₂]	64.7 (65.25)	9.0 (8.9)	2.7 (3.15)	4.7 (4.0)	7.0 (7.0)	
Non-metallated						
(7) [PdCl₂(qa)]	38.0 (38.0)	3.25 (2.9)	8.15 (8.05)	20.2 (20.4)		
(8) [PdCl₂(mqa)₂]	52.6 (52.8)	4.65 (4.45)	10.45 (10.25)	12.95 (13.0)		
(9) [PdCl₂(eqa)₂]	53.4 (54.4)	5.2 (4.9)	9.3 (9.75)	12.05 (12.35)		
(10) [PdCl₂(iqa)₂]	55.15 (55.85)	5.4 (5.35)	9.05 (9.3)	11.8 (11.8)		
(11) [PdCl₂(mqa)]	40.2 (39.85)	3.5 (3.35)	7.75 (7.75)	19.2 (19.6)		
(12) [Pd(O₂CMe)₂(mqa)₂]	55.85 (56.7)	3.35 (5.1)	9.55 (9.45)			
(13) [PdCl(dmp)(mqa)]	54.1 (54.8)	5.25 (5.25)	8.8 (9.15)	8.20 (7.7)		
(14) [Pd(NO₃)(dmp)(mqa)]	51.8 (51.8)	5.05 (4.95)	11.20 (11.5)			
(15) [PdCl(η-C₃H₅)(mqa)]	48.7 (49.05)	4.7 (4.65)	7.55 (7.65)	9.95 (9.65)		
(16) [Pd(η-C₃H₅)(mqa)][BF₄]	43.25 (43.05)	4.15 (4.1)	6.8 (6.1)			20.8 (5.14 × 10⁻³) 23.1 (2.57 × 10⁻³)
(17) [Pd(η-C₃H₅)(mqa)][ClO₄]	41.8 (41.8)	4.05 (3.95)	6.6 (6.5)	8.45 (8.2)		20.4 (3.92 × 10⁻³) 21.5 (1.96 × 10⁻³)
(18) [Pd(η-C₃H₅)(eqa)][BF₄]	44.15 (44.45)	4.5 (4.45)	6.55 (6.5)			21.2 (4.37 × 10⁻³) 24.1 (2.18 × 10⁻³)
(19) [Pd(η-C₃H₅)(eqa)][ClO₄]	43.0 (43.15)	4.5 (4.3)	6.2 (6.3)	8.15 (8.0)		21.2 (3.84 × 10⁻³) 22.9 (1.92 × 10⁻³)
(20) [Pd(η-C₃H₅)(iqa)][ClO₄]	44.45 (44.45)	4.55 (4.6)	6.2 (6.1)	7.9 (7.7)		21.1 (3.70 × 10⁻³) 22.7 (1.85 × 10⁻³)
(21) [Pd(η-C₃H₅)(qa)][ClO₄]	40.2 (40.4)	3.75 (3.4)	6.75 (6.75)	8.5 (8.5)		
(22) [Pd(η-C₄H₇)(mqa)][ClO₄]	43.0 (43.15)	4.4 (4.3)	6.25 (6.3)	8.05 (7.95)		19.5 (3.98 × 10⁻³) 21.1 (1.99 × 10⁻³)
(23) [Pd(η-C₄H₇)(eqa)][ClO₄]	44.55 (44.45)	4.75 (4.6)	6.3 (6.1)	7.5 (7.7)		21.9 (2.42 × 10⁻³) 22.3 (1.21 × 10⁻³)
(24) [Pd(η-C₃H₅)(mqa)₂][ClO₄]	52.2 (52.7)	4.9 (4.25)	9.0 (9.1)	6.55 (5.75)		
Metallated						
(25) [PdCl(mqa − H⁸)]	43.55 (44.35)	3.5 (3.4)	8.7 (8.6)	10.85 (10.9)		
(26) [PdCl(mqa − H⁸)(PEt₃)]	48.55 (48.75)	6.1 (5.9)	5.4 (6.3)	7.9 (8.0)	6.85 (7.0)	
(27) [Pd(O₂CMe)(mqa − H⁸)(OH₂)]	46.15 (45.85)	4.25 (4.4)	7.25 (7.65)			
(28) [{PdCl(mqa − H³)}₂]	44.85 (44.35)	3.45 (3.4)	8.45 (8.6)	9.85 (10.9)		
(29) [{Pd(O₂CMe)(eqa − H³)}₂]	49.25 (49.65)	4.5 (4.45)	7.6 (7.7)			
(30) [{PdCl(eqa − H³)}₂]	46.0 (46.05)	3.9 (3.85)	8.5 (8.25)	9.9 (10.45)		
(31) [{PdCl(iqa − H³)}₂]	47.1 (47.6)	4.1 (4.3)	7.85 (7.95)	10.55 (10.05)		
(32) [PdCl(mqa − H³)(NC₅D₅)]	49.75 (49.9)	4.0 (3.95)	9.8 (10.25)	9.3 (8.65)		
(33) [PdCl(eqa − H³)(NC₅D₅)]	50.5 (51.1)	4.4 (4.3)	9.7 (9.95)	8.85 (8.4)		
(34) [PdCl(iqa − H³)(NC₅D₅)]	52.0 (52.2)	4.4 (4.6)	9.35 (9.6)	8.5 (8.1)		

[a] Calculated values are given in parentheses. [b] Measured in nitrobenzene at 20 °C; concentrations (mol dm⁻³) are given in parentheses.

the bridge-splitting reactions (i)—(iii). The corresponding dichlorides [PdCl₂L₂] (L = mqa, eqa, or iqa), (8)—(10), are too insoluble for n.m.r. study but are presumed to be structurally equivalent to (12).

$$[Pd_3(O_2CMe)_6] + 6mqa \longrightarrow 3[Pd(O_2CMe)_2(mqa)_2] \quad (i)$$

$$[Pd_2Cl_2(dmp)_2] + 2mqa \longrightarrow 2[PdCl(dmp)(mqa)] \quad (ii)$$

$$[Rh_2Cl_2(cod)_2] + 2mqa \longrightarrow 2[RhCl(cod)(mqa)] \quad (iii)$$
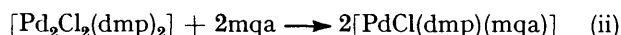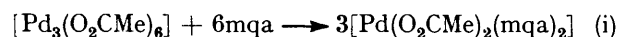
In compounds (4), (12), and (13) co-ordination of the imine NMe is indicated by n.m.r. shifts on co-ordination (downfield for NCH₃, NCH₃, and HC=N) (Tables 2 and 3), while the lack of co-ordination of the quinoline nitrogen is deduced from the negligible shift of the 8-Me signals (¹H or ¹³C n.m.r.). Bidentate (II), but not unidentate (I), co-ordination would bring the 8-R group close to the metal and result in n.m.r. co-ordination

shifts for this group. The marked downfield shift on co-ordination for the 3-H signals in the ¹H n.m.r. spectra of 3.09, 2.16, and 2.48 p.p.m. for (12), (13), and (4) respectively fully confirms that the configuration for (I) is as shown above. (A less remarkable but still significant shift is also found for the 3-C signal in the ¹³C n.m.r. spectrum.) Downfield shifts are expected for hydrogen atoms closely approaching d^8 square-planar metal atoms above the co-ordination plane, resulting from the magnetic anisotropy of the metal (see, for example, ref. 1). Thus we can clearly identify not only unidentate bonding but also the particular configuration which predominates in solution. With the *trans* configuration about the N=C bond a 180° rotation about the 2-quinolyl-to-CH=NMe bond would bring the quinolyl nitrogen atom close to the metal atom as required for bidentate bonding (II). It is the bulk of group R which

reduces the ability to rotate in this way to give bidentate co-ordination (II). The co-ordination of benzaldehyde-N-methylimine gives a system very comparable with

(I)

(II)

(III) mqa -H^3 (R =Me)
eqa - H^3 (R =Et)
iqa - H^3 (R =Pr^i)

(IV) mqa - H^8
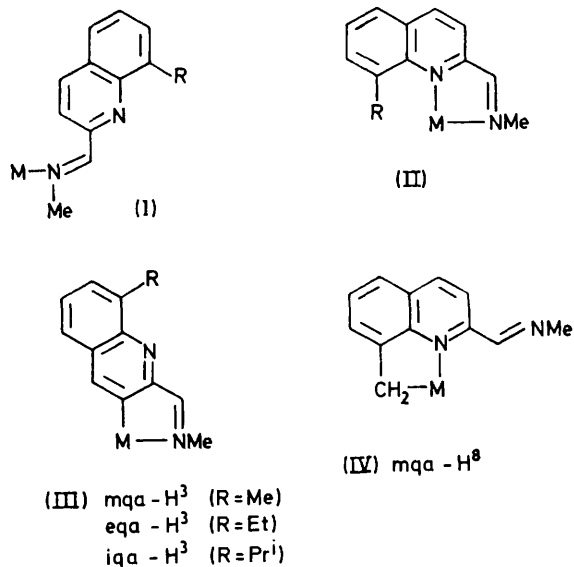
that described here, except that the downfield shift is shared between the 2- and 6-hydrogen atoms of the phenyl ring.[3] In this case ready rotation about the C_6H_5-CH=NMe bonds is possible, averaging the 2- and 6-H signals in the n.m.r. spectrum.

In compounds (4) and (13) the mqa ligands are fixed at room temperature in the configurations shown below. Three of the four possible ^{13}C signals for the co-ordinated atoms of C_8H_{12} [85.85, 84.80 p.p.m. (A and A$'$) and

(4)

(13)
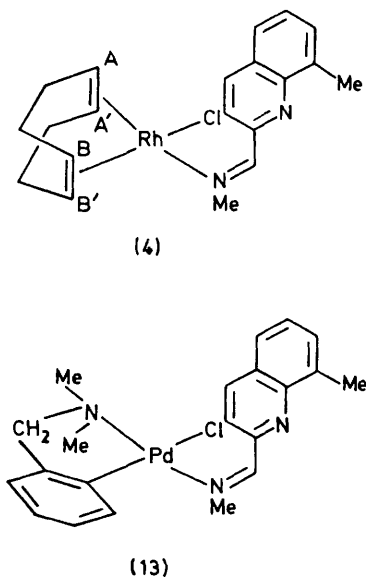
76.63 p.p.m. (B and B$'$) with relative intensity 1 : 1 : 2 respectively] are resolved for (4), and clearly separated NCH_3 signals and an AB quartet for the CH_2 group of the dmp ligand of (13) are observed in the n.m.r. spectra. The bulk of the mqa ligand in these two complexes must

remain on one side of the co-ordination plane on an n.m.r. time scale so as to retain these magnetic non-equivalences.

The unidentate behaviour of mqa in these compounds contrasts with the overriding tendency towards chelation for qa. Thus [PdCl$_4$]$^{2-}$ with an excess of qa in methanol gives the sparingly soluble yellow complex [PdCl$_2$(qa)] (7) containing bidentate qa and related to the sparingly soluble complexes [PdCl$_2$L] (L = 1,10-phenanthroline or 2,2$'$-bipyridyl).[4] Addition of mqa to [PdCl$_4$]$^{2-}$ in methanol, on the other hand, gives [PdCl$_2$(mqa)$_2$] (8) even when there is a deficiency of mqa. In an attempt to synthesise the mqa analogue of (7) we treated [PdCl$_2$(NCPh)$_2$] with mqa (1 : 1 mol ratio) and obtained the orange complex [PdCl$_2$(mqa)] (11) contaminated with (8) and separated from it by extraction with dichloro-methane. Unfortunately (11) is too insoluble for n.m.r. work. It may contain bidentate mqa, but of course might also be dimeric with chloro-bridges and uni-dentate mqa.

Compounds with Bidentate Co-ordination (II).—We have synthesised two series of complexes both containing bidentate mqa, eqa, or iqa.

Additions of mqa, eqa, or iqa to solutions of [Rh$_2$Cl$_2$-(CO)$_4$] in saturated hydrocarbons give yellow precipitates of complexes analysing for [RhCl(CO)$_2$L] [L = mqa (1), eqa (2), or iqa (3)] which are very soluble in chlorinated solvents. In contrast, qa gives an almost totally in-soluble dark coloured compound or mixture analysing approximately for [RhCl(CO)$_2$(qa)$_{0.75}$] but this was not characterised further. Bipyridyl and 1,10-phenanthro-line give similarly coloured materials.[5] Complexes (1)—(3) are structurely unrelated to (4) which clearly contains unidentate imine and we have the following evidence that they are five-co-ordinate with bidentate mqa, eqa, or iqa: (a) while the 8-CH_3 signal for (4) is at δ 17.84 p.p.m. compared with 17.78 p.p.m. for free mqa, the corresponding signal for (1) is at 19.90 p.p.m., indicating that the 8-Me group is sufficiently close to the metal to produce this downfield shift; (b) the 3-H signals are shifted hardly at all, being +0.02, +0.17, and +0.19 p.p.m. for (1), (2), and (3) respectively compared with the large downfield shift (−2.48 p.p.m.) of this signal for (4). A downfield shift (−0.6 p.p.m.) was also observed with [RhCl(CO)$_2$(4-MeC$_6$H$_4$CH=NMe)] [3] (in which case the downfield shift is averaged between the 2- and 6-H atoms) so that close approach of hydrogen atoms to the metal should produce downfield shifts with the dicarbonyl as well as cyclo-octadiene complexes. The 3-H is clearly well removed from the rhodium atom in (1)—(3).

The observations (a) and (b) are only consistent with bidentate co-ordination and the single sharp sets of ligand ^{1}H and [13]C n.m.r. signals suggest that a single species is present in solution. However, solution i.r. spectra around 2 000 cm^{-1} require two *cis*-dicarbonyl complexes to be present in solution (Figure 1 and Table 4), the relative concentration of which depends on the solvent, as shown by the increase or decrease in intensity

TABLE 2

Selected ¹H n.m.r. data [a]

Compound		H³	H⁴	CH=N	NCH₃	8-R	Other resonances
				mqa, eqa, or iqa resonances			
mqa		8.07 (s)	8.07 (s)	8.57 (q)	3.59 (d)	2.81 (s)	
eqa		8.07 (s)	8.07 (s)	8.56 (q)	3.59 (d)	3.31 (q), 1.38 (t)	
iqa		8.07 (s)	8.07 (s)	8.55 (q)	3.59 (d)	4.43 (sp), 1.39 (d)	
(1)	(20 °C)	8.09 (d)	8.37 (d)	8.69 (q)	3.96 (d)	3.05 (s)	
	(−60 °C)	8.24 (d)	7.98 (d)	8.75 (br)	4.02 (br)	3.14 (s)	
(2)	(20 °C)	8.24 (d)	8.48 (d)	8.66 (br)	3.96 (br)	3.64 (q), 1.43 (t)	
	(−60 °C)	8.11 (s)	8.11 (s)	8.67 (br)	3.98 (br)	3.74 (m), 1.45 (br t)	
(3)	(20 °C)	8.26 (d)	8.46 (d)	8.68 (q)	3.95 (d)	5.06 (sp), 1.40 (d)	
	(−60 °C)	8.13 (d)	8.21 (d)	8.70 (br)	4.00 (br)	5.32 (br m). 1.42 (br)	
(4)		10.55 (d)	8.49 (d)	8.57 (br)	3.98 (br)	2.82 (s)	C₈H₁₂: 4.57, 3.57, 2.48, 1.82 (all br)
(5)			8.00 (s)	8.65 (br)	4.19 (br)	2.74 (s)	IrH: −19.21 (t), J(PH) 19.0 P(C₆H₁₁)₃: 1—2
(6)			7.90 (s)	8.61 (br)	4.10 (br)	2.73 (s)	RhH: −15.29 (q), J(PH) = J(RhH) 15.5 P(C₆H₁₁)₃: 1—2
(12)		11.16 (d)	8.58 (d)	8.18 (q)	4.00 (d)	2.76(s)	CH₃CO₂: 1.52 (s)
(13)		10.23 (d)	8.03 (d)	8.30 (q)	4.11 (d)	2.81 (s)	NCH₃: 2.96 (br s); NCH₂: 4.11, 3.77 (AB quartet); H: 6.48 (d)
(17)		8.03 (d)	8.69 (d)	9.04 (br)	4.00 (br)	2.83 (s)	C₃H₅: 3.18 (d), 3.31 (d), 4.13 (d), 4.25 (d), 5.68 (m)
(19)		8.11 (d)	8.71 (d)	9.05 (br)	4.00 (br)	3.68 (br m) [c], 1.08 (br t)	C₃H₅: 3.17 (d), 3.30 (d), 3.95 (d), 4.24 (d), 5.70 (m)
(20)	(−80 °C) [b] CD₂Cl₂	8.15 (d)	8.74 (d)	9.08 (q)	4.02 (d)	4.78 (m), 1.28 (br)	C₃H₅: 3.18 (d), 4.42 (d), 3.92 (d), 4.30 (d), 5.80 (m)
(22)		8.06 (d)	8.68 (d)	9.02 (br)	3.99 (br)	2.88 (s)	C₄H₇: 2.24 (s), 3.01 (s), 3.14 (s), 3.90 (s), 3.99 (s)
(23)		8.13 (d)	8.74 (d)	9.06 (q)	4.00 (d)	3.34 (br m),[d] 3.70 (br m),[d] 1.07 (br t)	C₄H₇: 2.25 (s), 3.02 (s), 3.13 (s), 3.80 (s), 4.00 (s)
(26)		8.24 (s)	8.24 (s)	9.56 (q)	3.66 (d)	3.16 (d) [e]	
(27)		7.77 (d)	7.97 (d)	8.58 (q)	3.62 (d)	3.33 (s)	CH₃CO₂: 2.10 (s)
(29)			7.57 (s)	7.61 (q)	3.02 (d)	3.18 (q), 1.32 (t)	CH₃CO₂: 2.23 (s)
(32)			6.72 (s)	8.10 (q)	3.73 (d)	2.76 (s)	
(33)			6.71 (s)	7.88 (br)	3.64 (br)	3.25 (q), 1.36 (t)	
(34)			6.74 (s)	8.06 (br)	3.70 (br)	4.26 (sp), 1.32 (d)	

[a] Chemical shift δ/p.p.m., J in Hz. Spectra recorded on a Varian HA100 spectrometer at 100 MHz in CDCl₃ at 27 °C unless stated otherwise. Coupling of 1—2 Hz between CH and CH₃ of the imine is observed in all cases. = S singlet, d = doublet, t = triplet, q = quartet, sp = septet, m = multiplet, br = broad. [b] At room temperature coalescence of the two syn-hydrogen doublets (δ ca. 3.2 and 3.3) and of the two anti-hydrogen doublets (δ ca. 4.0 and 4.3) of the η-C₃H₅ had occurred. Similar coalescences of the appropriate η³-C₄H₇ singlets also occurs. [c] At room temperature the CH₂CH₃ signal is a quartet at δ 3.42 p.p.m. which broadens and separates into two broad multiplets at −80 °C, one at δ 3.68 p.p.m., the other obscured by C₃H₅ signals. [d] The broad multiplets at δ 3.34 and 3.70 p.p.m. coalesce to give a quartet at δ 3.45 p.p.m. at room temperature. [e] J(P–CH₂) 2.9 Hz; signal intensity equivalent to 2 H and coupling to ³¹P indicates metallation at 8-CH₃.

of pairs of the four ν(CO) absorptions with change of solvent. The relative concentration of the two species does not, however, depend on the 8-R group since the spectra of (2) and (3) in CHCl₃ are almost indistinguishable from that for (1) in the same solvent [Figure 1(c)]. The shift in wavenumber with solvent is up to 12 cm⁻¹ while the separation of the appropriate pairs of absorp tions is always in the range 72—76 cm⁻¹. The two ν(CO) absorptions for square-planar cis-rhodium dicarbonyls are usually separated by ca. 75 cm⁻¹ so the angle between the CO ligands must also be about 90° in (1)—(3). We propose that there are two isomers (V) and (VI) for each compound (1)—(3) which rapidly interconvert in solution to give single sets of ¹H and ¹³C n.m.r. signals but separate i.r. absorptions. N.m.r. spectra could not be frozen out at −60 °C but chemical-shift changes with temperature for the mqa, eqa, and iqa signals (Table 2)

are somewhat greater than expected unless the ratio of isomer (V) to (VI) also varies with temperature. Figure 2 illustrates the structures we propose, isomers (V) and (VI) being the same except for the direction of tilt of the chelate ring. We have no evidence for a tilt in these compounds but there is a marked tilt in the complex [Pd(η³-allyl)(iqa)][ClO₄] as described below.

Other complexes containing bidentate mqa, eqa, or iqa ligands of the type [Pd(η³-allyl)L]X (allyl = allyl or 2-methylallyl; L = mqa, eqa, or iqa; X = ClO₄ or BF₄) are readily synthesised as yellow crystals, readily soluble in chloroform. The corresponding ligand which is unsubstituted at the 8-position gives a product with a directly corresponding formula, [Pd(η-C₃H₅)(qa)][ClO₄], but which is insoluble and colourless. The different physical properties imply structural changes going from qa, which can adopt bidentate co-ordination without

steric hindrance, to mqa, eqa, or iqa where we envisaged originally that the R group would clash considerably with the η³-allyl. Applying the same n.m.r. criteria as for [RhCl(CO)₂L], we showed that mqa, eqa, and iqa are bidentate. One way to alleviate the clash of R with the η³-allyl would be to convert this into a σ-allyl [Figure 3, (VIII)]. The n.m.r. spectra, however, clearly show η³-allyls and furthermore a molecule of structure (VIII) must be significantly higher in energy than (VII) since terminal *syn* and *anti* hydrogens of the allyl give separate ¹H n.m.r. signals at room temperature whereas a rapid equilibrium of type (VII) ⇌ (VIII) would lead to coalesced signals. A dynamic n.m.r. process that is observed is the exchange of the non-equivalent terminal allyl carbons. Figure 4 illustrates that at 20 °C the

signals due to Cᴬ and Cᶜ have coalesced while being resolved at −80 °C. This results from the effective interchange of the co-ordination sites of the two nitrogen atoms and it is likely that this occurs *via* a unidentate mqa intermediate but this has not been established. For the iqa complex the non-equivalent isopropyl methyl groups are similarly coalesced at 20 but not at −80 °C and a similar effect is found for the CH₂CH₃ signals for the eqa complex. Thus, as well as interchange of the terminal sites of the η³-allyl, there is a time-averaged plane of symmetry generated through the quinolyl group by the dynamic process(es).

Having established the bidentate nature of mqa, eqa, and iqa in solutions of complexes (16)—(23), the problem remained of why the clash of the 8-R group with the

TABLE 3

Carbon-13 n.m.r. data [a]

mqa, eqa, or iqa resonances

Compound	C²	C⁹	C⁴	C⁸	C³	C¹⁰	C⁵	C⁶	C⁷	8-R	C=N	NCH₃	Other resonances
mqa	153.7	146.8	136.4	137.7	117.7	128.6	125.5	126.9	129.6	17.8	164.5	48.0	
eqa	153.5	146.1	136.5	143.4	117.6	128.6	125.5	127.1	128.0	24.4, 15.1	164.7	48.0	
iqa	153.5	145.6	136.7	147.9	117.5	128.7	125.4	125.4	127.3	27.2, 23.5	164.9	48.1	
(1)	148.7	147.0	137.4	138.5	122.6	129.2	125.8	128.8	131.0	19.9	170.6	51.7	
(2)	148.1	146.2	137.6	143.9	123.0	129.2	125.6	129.0	129.1	25.2, 15.4	170.3	52.1	
(3)	148.1	145.5	137.8	148.5	122.8	129.1	125.5	126.7	129.1	26.9, 23.8	170.4	52.1	
(4)	151.1	146.6	136.9	137.8	121.2	128.9	125.8	128.2	130.3	17.8	169.6	52.0	C₈H₁₂: 31.1, 30.6, 85.8 (J 10.7), 84.8 (J 11.2), 76.6 (J 13.8)
(5)	165.9	143.3	144.7	137.3	138.7 [b]	126.5	123.3	125.8	130.3	18.0	176.4	46.4	P(C₆H₁₁)₃: 34.1 (J 12.8), 29.1, 27.5, 26.9
(6)	163.2	143.7	145.9	137.2	159.5 [c]	126.5	123.4	126.5	129.3	18.0	174.5	46.3	P(C₆H₁₁)₃: 34.4 (J 9.8), 29.4, 27.7, 26.9
(12)	150.3	146.7	137.1	138.0	120.7	129.1	125.8	128.2	130.0	17.8	171.9	51.7	CH₃CO₂: 22.2, 178.4
(13) [d]	{150.5	146.7	146.2	137.9	136.2	130.0	128.2	125.5	119.9}	17.8	169.7	52.5	NMe₂: 52.7, 53.8 NCH₂: 73.8
(17) [e]	153.7	148.6	142.9	142.9	122.1	131.0	126.8	129.4	134.9	19.4	170.0	52.3	C₃H₅: 117.4 (central), 60.3, 69.2 (terminal)
(19) [e]	153.8	147.4	142.9	141.8	122.2	131.2	126.8	129.9	133.8	25.9, 17.7	170.1	52.3	C₃H₅: 117.6 (central), 60.4, 69.3 (terminal)
(20) [e]	153.5	146.9	143.0	145.8	122.2	131.3	126.5	129.3	129.7	28.9, 23.2 [f], 23.7 [f]	170.1	52.2	C₃H₅: 117.7 (central), 61.2,[f] 67.6 [f] (terminal)
(26)	151.5	149.4	138.6	148.7	121.7 [g]	129.7	123.8	129.7	130.3	24.7 [h]	168.7	49.8	PEt₃: 15.4 (J 29.5), 8.6
(27)	149.6	150.3	135.9	149.9	121.9	129.8	123.2	129.8	130.7	23.5	164.6	47.8	CH₃CO₂: 22.6, 179.2
(32)	164.7	144.9	137.7	137.8	164.5	128.5	124.8	127.7	128.5	17.8	176.6	49.6	
(33	164.7	144.3	137.7	143.8	146.4	128.6	124.8	126.7	127.9	24.3, 15.2	176.7	49.6	
(34)	164.6	143.7	137.8	148.2	146.2	128.7	124.1	124.6	128.0	27.2, 23.6	176.8	49.5	

	C²		C⁶		C¹		C³	C⁴	C⁵				
4-MeC₆H₄ [i] CH=NMe	133.7		129.3		127.9		127.9	129.3	129.3		162.3	48.1	4-Me: 21.4
(35)	143.9		132.8		157.7		125.2	126.9	140.8		175.5	48.8	4-Me: 22.1

[a] Recorded in CDCl₃ at 23 °C on a Varian CFT 20 spectrometer at 20 MHz; in p.p.m. downfield from internal SiMe₄, J in Hz. Assignments have not been made for signals with shifts given in parentheses. [b] Triplet; J(P–C³) 7.7 Hz. [c] Double triplet; J(P–C³) 9.8, J(Rh–C³) 34.7 Hz. [d] The C₆H₄ signals of the dmp ligand are at 147.16, 131.26, 128.81, 125.10, 124.49, and 121.16 p.p.m. [e] Spectra recorded in CD₂Cl₂ at −80 °C. At room temperature the terminal allyl carbon signals and the Prⁱ signals had coalesced. [f] Signals broad due to incomplete freezing out of exchange. [g] Doublet; J(P–C³) 1.4 Hz. [h] Palladium-bound CH₂; doublet, J(P–C) 5.6 Hz. [i] Signals for C¹, C², C⁶ under corresponding signals for mqa, eqa, and iqa.

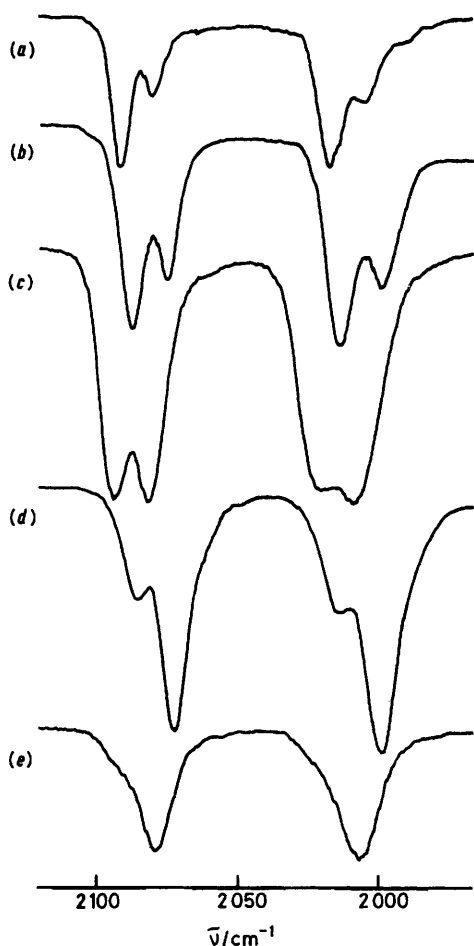Assignments:
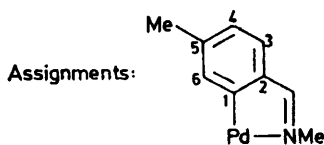
FIGURE 1 ν(CO) spectra for complex (1) in different solvents: (a) C_6H_{12}, (b) diethyl ether, (c) $CHCl_3$, (d) acetone, and (e) MeOH

η^3-allyl did not prevent their formation. Addition of an excess of mqa to complex (17) gives $[Pd(\eta\text{-}C_3H_5)(mqa)_2]$-$[ClO_4]$ (24) containing unidentate mqa, as does complex $[PdCl(\eta\text{-}C_3H_5)(mqa)]$ (15), but (24) can only be crystal-lised from solutions containing free mqa and on re-dissolving dissociation to complex (17) and mqa occurs. Hence the complex with bidentate mqa is relatively stable. To help understand these observations a single-crystal X-ray diffraction study of $[Pd(\eta\text{-}C_3H_5)(iqa)]$-$[ClO_4]$ (20) was carried out and the results confirmed bidentate co-ordination but with novel features. Figure 5 shows the structure of the $[Pd(\eta\text{-}C_3H_5)(iqa)]^+$ cation,

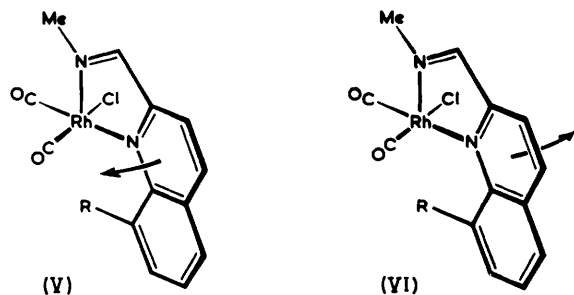FIGURE 2 Proposed structures for complexes (1)—(3)

TABLE 4

Infrared data (cm⁻¹) for rhodium dicarbonyl complexes (1)—(3) *

Compound	Solvent	ν(CO) Isomer (V)	Isomer (VI)
(1)	C_6H_{12}	2 091, 2 018	2 080, 2 006
	OEt_2	2 087, 2 014	2 075, 1 999
	$CHCl_3$	2 092, 2 020	2 080, 2 009
	CH_3COCH_3	2 086, 2 014	2 073, 1 999
	MeOH	2 092, (sh),	2 079, 2 007
		2 020, (sh),	
(2)	$CHCl_3$	2 092, 2 020	2 080, 2 009
(3)	$CHCl_3$	2 092, 2 019	2 080, 2 009

* It is assumed that the lower-frequency pair of absorptions belong to the same isomer. A single ν(Rh–Cl) absorption was observed for each in the solid state at 299, 304, and 302.5 cm⁻¹ for (1), (2), and (3) respectively. Single ν(M–Cl) absorptions were also observed for (4) (278), (8) (331), (9) (329), and (10) (329 cm⁻¹).

and the atom-labelling scheme used. The $[ClO_4]^-$ anion, not shown in the Figure, is disordered over two orientations (see Experimental section) and has distorted tetrahedral geometry but without any significantly close contact with the cation. Important interatomic dist-ances and interbond angles are given in Table 5 while
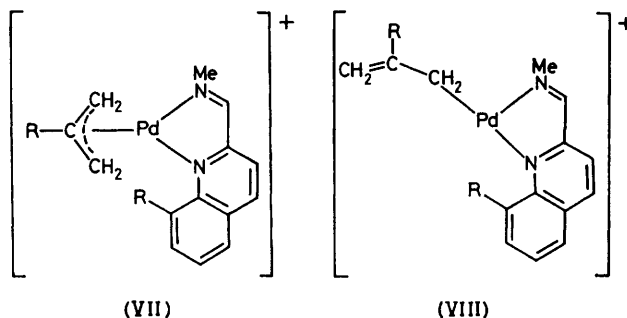
FIGURE 3 Structures considered for complexes (16)—(23)
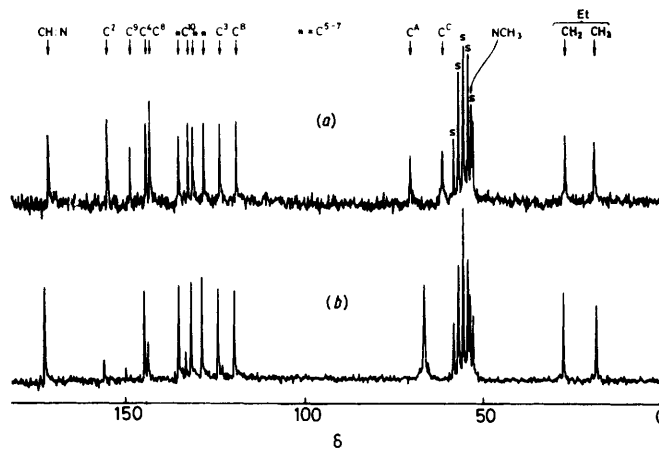
FIGURE 4 Carbon-13 n.m.r. spectra for complex (19), [Pd-$(\eta\text{-}C_3H_5)(eqa)][ClO_4]$, at (a) −80 and (b) 20 °C; the C_3H_5 carbon atoms are labelled, C^A, C^B, and C^C

selected least-squares planes and dihedral angles are given in Table 6.

Both nitrogen atoms are co-ordinated to the palladium atom [Pd–N(1) (quinoline) 2.184(3) Å and Pd–N(2) (imine) 2.079(4) Å] and the η^3-allyl is normal. The allyl

FIGURE 5 Structure of $[Pd(\eta\text{-}C_3H_5)(iqa)]^+$ showing the atom-labelling scheme

is tilted away from a perpendicular orientation to the co-ordination plane with a dihedral angle of 127.9° between the PdN(1)N(2) and the C(16)C(17)C(18) planes.

TABLE 5

Selected interatomic distances (Å) and angles (°), with estimated standard deviations (e.s.d.s) in parentheses

(a) Distances in $[Pd(\eta\text{-}C_3H_5)(iqa)]^+$

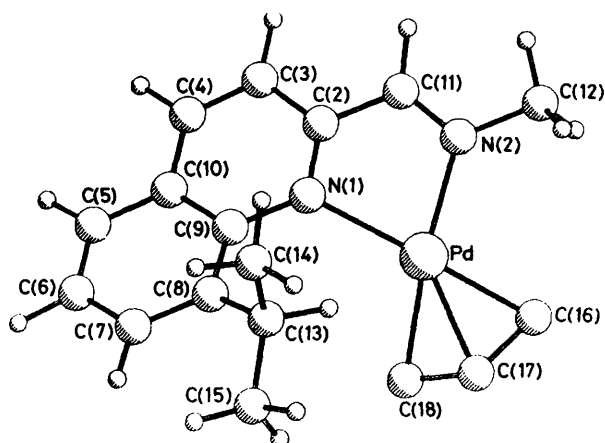|			
Pd–N(1)	2.184(3)	C(6)–C(7)	1.410(8)
Pd–N(2)	2.079(4)	C(7)–C(8)	1.378(6)
Pd–C(16)	2.102(6)	C(8)–C(9)	1.413(6)
Pd–C(17)	2.116(8)	C(9)–C(10)	1.429(6)
Pd–C(18)	2.153(7)	C(2)–C(11)	1.442(7)
		N(2)–C(11)	1.273(7)
N(1)–C(2)	1.328(6)	N(2)–C(12)	1.470(8)
N(1)–C(9)	1.376(5)	C(8)–C(13)	1.519(6)
C(2)–C(3)	1.412(7)	C(13)–C(14)	1.532(7)
C(3)–C(4)	1.334(8)	C(13)–C(15)	1.531(9)
C(4)–C(10)	1.413(9)		
C(5)–C(6)	1.342(9)	C(16)–C(17)	1.389(12)
C(5)–C(10)	1.394(8)	C(17)–C(18)	1.323(10)

(b) Angles in $[Pd(\eta\text{-}C_3H_5)(iqa)]^+$

N(1)–Pd–N(2)	77.7(2)	N(1)–C(2)–C(3)	122.9(4)
N(1)–Pd–C(16)	170.1(2)	N(1)–C(2)–C(11)	116.5(4)
N(1)–Pd–C(17)	141.8(2)	C(3)–C(2)–C(11)	120.6(5)
N(1)–Pd–C(18)	108.6(2)	C(2)–C(3)–C(4)	118.6(5)
N(2)–Pd–C(16)	103.4(2)	C(3)–C(4)–C(10)	120.5(5)
N(2)–Pd–C(17)	140.5(3)	C(6)–C(5)–C(10)	119.9(5)
N(1)–Pd–C(18)	163.7(2)	C(5)–C(6)–C(7)	120.8(5)
C(16)–Pd–C(17)	38.4(3)	C(6)–C(7)–C(8)	122.4(5)
C(16)–Pd–C(18)	67.7(3)	C(7)–C(8)–C(9)	116.5(4)
C(17)–Pd–C(18)	36.1(3)	C(7)–C(8)–C(13)	122.5(4)
		C(9)–C(8)–C(13)	120.3(4)
Pd–N(1)–C(2)	106.2(3)	C(8)–C(9)–C(10)	120.4(4)
Pd–N(1)–C(9)	129.2(3)	C(8)–C(9)–N(1)	120.6(4)
C(2)–N(1)–C(9)	119.4(3)	C(10)–C(9)–N(1)	118.9(4)
		C(4)–C(10)–C(5)	121.9(5)
Pd–N(2)–C(11)	111.8(3)	C(4)–C(10)–C(9)	118.5(4)
Pd–N(2)–C(12)	127.7(4)	C(5)–C(10)–C(9)	119.4(5)
C(11)–N(2)–C(12)	119.6(5)	C(2)–C(11)–N(2)	119.6(4)

(c) Geometry of the $[ClO_4]^-$ group

Orientation (1)		Orientation (2)	
Cl–O(1)	1.387(14)	Cl–O(2)	1.311(19)
Cl–O(3)	1.442(11)	Cl–O(5)	1.241(19)
Cl–O(4)	1.505(13)	Cl–O(7)	1.298(22)
Cl–O(6)	1.314(15)	Cl–O(8)	1.573(27)
O(1)–Cl–O(3)	105.2(8)	O(2)–Cl–O(5)	111.3(1.2)
O(1)–Cl–O(4)	102.9(8)	O(2)–Cl–O(7)	111.7(1.3)
O(1)–Cl–O(6)	116.5(1.1)	O(2)–Cl–O(8)	100.3(1.3)
O(3)–Cl–O(4)	100.8(7)	O(5)–Cl–O(7)	127.6(1.6)
O(3)–Cl–O(6)	120.5(1.2)	O(5)–Cl–O(8)	98.7(1.2)
O(4)–Cl–O(6)	108.4(1.1)	O(7)–Cl–O(8)	101.6(1.5)

TABLE 6

Least-squares planes in the form $Ax + By + Cz = D$, where x,y,z, are fractional co-ordinates. Deviations (Å × 10³) of relevant atoms are given in square brackets

Plane (1): Pd, N(1), N(2)

$$8.116x - 2.545y - 3.632z = 3.274$$

[C(2) −539, C(3) −1 222, C(4) −1 422, C(5) −946, C(6) −264, C(7) 615, C(8) 787, C(9) −24, C(10) −834, C(11) −397, C(12) 175, C(13) 1 921, C(14) 3 109, C(15) 2 378, C(16) −360, C(17) 60, C(18) −548, H(13) 1 650]

Plane (2): N(1), C(2) , C(3), C(4), C(10), C(9)

$$5.484x - 6.073y + 3.049z = 2.445$$

[Pd −1 092, N(1) −46, C(2) −11, C(3) 50, C(4) −30, C(10) −27, C(9) 65]

Plane (3): N(1), C(2)—C(10)

$$5.034x - 6.038y + 4.497z = 2.683$$

[Pd −1 269, N1( ) −141, N(2) −394, C(2) −11, C(3) 134, C(4) 36, C(5) −71, C(6) −31, C(7) 81, C(8) 113, C(9) −51, C(10) −61, C(11) −24, C(12) −379, C(13) 514, C(14) 2 017, C(15) 194, C(16) −2 640, C(17) −2 497, C(18), −2 686, H(13) 79]

Plane (4): N(2), C(11), C(12)

$$6.930x - 4.805y - 1.461z = 1.911$$

[Pd −335, N(1) 317, C(2) 31, C(3) −235, C(4) −300, C(5) 70, C(6) 521, C(7) 1 022, C(8) 1 035, C(9) 447, C(10) 37]

Plane (5): C(16), C(17), C(18)

$$-3 137x - 7.107y - 7.564z = 1.048$$

Angles (°) between normals to planes:

(1)–(2)	33.3	(1)–(5)	127.9
(1)–(3)	37.4	(2)–(4)	15.6
(1)–(4)	18.3		

Selected torsion angles (°). The sign of the angle A–B–C–D is positive when a clockwise rotation about B–C is required to bring A–B–C into coincidence with B–C–D, viewed along B–C

A	B	C	D	
N(2)–Pd–N(1)–C(2)				25.0
N(2)–Pd–N(1)–C(9)				178.7
N(1)–Pd–N(2)–C(11)				−19.6
N(1)–Pd–N(2)–C(12)				171.4
Pd–N(1)–C(2)–C(3)				152.6
Pd–N(1)–C(2)–C(11)				−27.4
C(9)–N(1)–C(2)–C(3)				−4.2
C(9)–N(1)–C(2)–C(11)				175.9
Pd–N(1)–C(9)–C(8)				43.4
Pd–N(1)–C(9)–C(10)				−139.6
C(2)–N(1)–C(9)–C(8)				−165.8
C(2)–N(1)–C(9)–C(10)				11.2
Pd–N(2)–C(11)–C(2)				11.4
C(12)–N(2)–C(11)–C(2)				−178.6
N(1)–C(2)–C(3)–C(4)				−5.1
C(11)–C(2)–C(3)–C(4)				174.8
N(1)–C(2)–C(11)–N(2)				12.6
C(3)–C(2)–C(11)–N(2)				−167.3
C(2)–C(3)–C(4)–C(10)				6.9
C(3)–C(4)–C(10)–C(5)				175.5
C(3)–C(4)–C(10)–C(9)				0.0
C(10)–C(5)–C(6)–C(7)				2.9
C(6)–C(5)–C(10)–C(4)				−173.4
C(6)–C(5)–C(10)–C(9)				2.0
C(5)–C(6)–C(7)–C(8)				−2.1
C(6)–C(7)–C(8)–C(9)				−3.5
C(6)–C(7)–C(8)–C(13)				167.2
C(7)–C(8)–C(9)–N(1)				−174.7
C(7)–C(8)–C(9)–C(10)				8.3
C(13)–C(8)–C(9)–N(1)				14.3
C(13)–C(8)–C(9)–C(10)				−162.7
C(7)–C(8)–C(13)–C(14)				−92.6
C(7)–C(8)–C(13)–C(15)				29.0
C(9)–C(8)–C(13)–C(14)				77.9
C(9)–C(8)–C(13)–C(15)				−160.6
N(1)–C(9)–C(10)–C(4)				−9.2
N(1)–C(9)–C(10)–C(5)				175.2
C(8)–C(9)–C(10)–C(4)				167.8
C(8)–C(9)–C(10)–C(5)				−7.8

This is normal for η³-allyl complexes of palladium.[6] Carbon-13 and ¹H n.m.r. results indicate an asymmetric η³-allyl, with a ¹³C shift of 6.42 p.p.m. between the terminal carbon atoms *trans* to the quinoline and the imine nitrogen atoms respectively. Rather greater separations are found for the mqa complex (17) (8.88 p.p.m.) and the eqa complex (19) (8.90 p.p.m.). The geometric asymmetry of the allyl is, however, not great; the C–C distances within the allyl are 1.389(12) [C(16)–C(17)] and 1.323(10) Å [C(17)–C(18)], the shorter C–C distance being associated with slightly longer Pd–C distances [Pd–C(16) 2.102(6) and Pd–C(18) 2.153(7) Å]. This is consistent with a greater *trans* influence for the imine compared with the quinoline nitrogen and the bond-length variations are related to those found in [PdCl(η³-allyl)(PPh₃)] in which PPh₃ has a greater *trans* influence than Cl.[7,8]
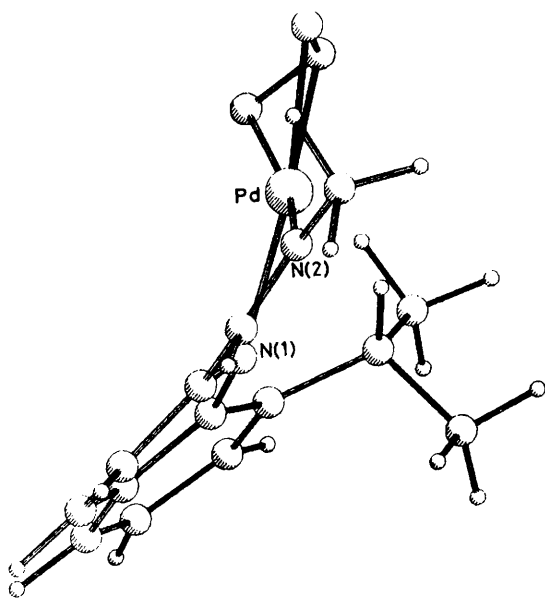

FIGURE 6 Displacement of the iqa ligand out of the co-ordination plane in [Pd(η-C₃H₅)(iqa)]⁺

The most important structural feature of compound (20) is the twisting of the iqa ligand with respect to the co-ordination plane to reduce the expected close approach of the Prⁱ group to the allyl group and the Pd atom. The closest non-bonded contact between the metal atom and the Prⁱ group is the Pd · · *H*CMe₂ contact of 2.44 Å. To achieve this distance the iqa ligand and the geometry of its co-ordination are severely distorted as can be seen in Figure 6. The gross distortion can be discussed in terms of a number of contributing features. Atom N(2) has a small pyramidal distortion (sum of its three angles = 358°) so that the Pd–N(2) bond makes an angle of 9.3° with the CH=NC(Me) plane with the metal atom 0.335 Å out of this plane; N(1) has suffered a large pyramidal distortion (sum of angles = 354°) so that the Pd atom lies 1.09 Å out of the plane of the six-membered ring containing N(1). The severe twisting of the ligand is best expressed in terms of the torsional

angles for C(2)N(1)C(9)C(8), 14.2°, and N(1)C(9)C(8)C(13), 14.3°, and the end result is summarised by the deviations of individual atoms from the best plane of the quinoline system [plane (2), Table 6].

Of all the above distortions the pyramidality of N(1) is worthy of extra comment. In square-planar complexes of pyridine and related ligands the greatest structural flexibility results from rotation about the M–N bond and dihedral angles between the ligand and co-ordination planes ranging from 17.2° (ref. 9) to *ca.* 90° (ref. 1) have been reported. Tilting of the M–N bond within the ligand plane is also quite common and we have observed Pd–N–C angles of 111 and 131° in a 7,8-benzoquinoline complex,[1] but this is the first clear report of a considerable tilting of the M–N bond out of the ligand plane. Tris(2-pyridyl)triazine has been shown to co-ordinate somewhat like iqa in (20), *i.e.* steric interaction forces a pyramidal arrangement at one nitrogen atom, but this is so far removed from the metal (2.75 Å) that it should perhaps be regarded as unco-ordinated.[10]

If the pyramidal arrangement about N(1) is achieved by forming a ' bent ' Pd–N bond one would expect N(1) to be positioned out of an idealised co-ordination plane in the direction of the quinoline tilt. There is, however, no rotation of the η³-allyl about the allyl–palladium axis to support this; if anything the displacement is opposite to the expected direction with C(16) 0.360 Å and C(18) 0.548 Å out of the PdN₂ plane. An alternative description is that N(1) is rehybridised from sp^2 towards sp^3, but there is no evidence for N(1)C(9) and N(1)C(2) bond lengthening nor any abnormal n.m.r. shifts that might result from disturbance of the π overlap of the ring at N(1). Whatever the most appropriate description of the Pd–N(1) bond, it is important to recognise that a significantly non-planar geometry at a donor pyridine or quinoline nitrogen atom is possible without great weakening of the M–N bond.

One other structural feature of note is the Pd · · H contact of 2.44 Å. Realising that this distance is achieved *after* the ligand has undergone its severe distortion, it is interesting to compare the structure of the present molecule with that of the 7,8-benzoquinoline complex cation[1] mentioned above in which a hydrogen atom of the unidentate benzoquinoline ligand makes a close Pd · · · H contact of 2.09 Å. In this case, however, the hydrogen atom is placed in an ' axial ' position with respect to the co-ordination plane. Possible explanations for the difference between the Pd · · · H contacts could be that the van der Waals radius for the palladium atom varies with direction, being very short in a direction perpendicular to the co-ordination plane, or that the shorter Pd · · · H contact in the benzoquinoline complex[1] is a bonding interaction after all, but a third and likely explanation is that chelation of iqa allows more extensive distortion of the co-ordinative bonding and so more effectively relieves the Pd · · · H clash without destabilising the complex excessively.

Metallation Products of Type (III) *and* (IV).—Mqa is an interesting ligand in that metallation may occur at the

3-position of the quinoline or at the 8-methyl group. Oxidative addition to Rh^I or Ir^I using the system developed by Vrieze and co-workers [3] is at the 3-position. Thus treatment of [{MCl(C$_8$H$_{14}$)$_2$}$_2$] (M = Rh or Ir; C$_8$H$_{14}$ = cyclo-octene) with tricyclohexylphosphine and
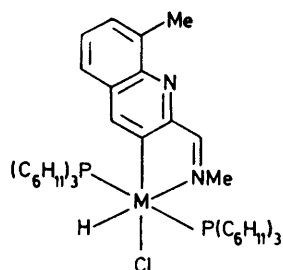

(5) M = Ir

(6) M = Rh

mqa in refluxing benzene gives [MH(Cl)(mqa — H^3)-{P(C$_6$H$_{11}$)$_3$}$_2$], compounds (5) and (6). The presence of hydride ligands was easily confirmed by ^{1}H n.m.r. (Table 2) and the observation of ν(M–H) at 2 182 cm^{-1} (Rh) and 2 240 cm^{-1} (Ir). The site of metallation at mqa was established by the loss of the 3-H n.m.r. signal and the appearance of 4-H singlets for these compounds. The ^{13}C n.m.r. signals for the carbon atoms of the chelate ring are all shifted downfield, notably the metal-bound carbon signal which is shifted 41.8, 21.0, and 28.9 p.p.m. respectively in the rhodium and iridium complexes and in the 3-metallated palladium complex (32) described below. The order of downfield shifts Rh > Pd > Ir is expected. The 8-methyl signals in the ^{13}C and ^{1}H n.m.r. are unshifted. Based on spectroscopic evidence the structures of (5) and (6) are as shown.

In marked contrast, metallation of mqa with palladium acetate occurs exclusively at the 8-Me group. The initial product appears to be [Pd(O$_2$CMe)(mqa — H^8)-(OH$_2$)] (27), but treatment with chloride ions and PEt$_3$ gave the unambiguously characterised complex [PdCl-(mqa — H^8)(PEt$_3$)] (26). The palladium-bound CH$_2$ group gives doublets (^{31}P coupling) in the ^{1}H and ^{13}C (proton-decoupled) n.m.r. spectra consistent with the configuration shown. Under decoupler-offset conditions the ^{13}C n.m.r. signal is a triplet of doublets, confirming that only two hydrogen atoms remain on the 8-substituent.


(25)   (26)
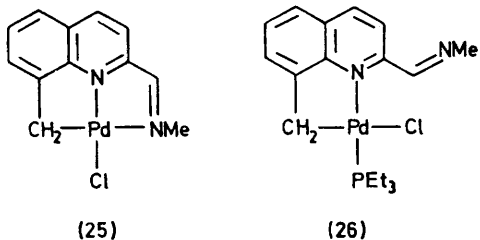
A competition between metallation at these two sites occurs when mqa is treated with Na$_2$[PdCl$_4$] in refluxing methanol. The yellow precipitate is a mixture of isomers which may be separated by Soxhlet extraction (CH$_2$Cl$_2$) of an orange, slightly soluble, component [PdCl(mqa — H^8)] (25) which gave complex (26) on treatment with PEt$_3$. The latter complex is identical spectroscopically with that derived from palladium acetate. The component which remains as a yellow powder after CH$_2$Cl$_2$ extraction analyses as [PdCl-(mqa — H)] (28) and was characterised by treatment with [^{2}H$_5$]pyridine to give the complex [PdCl(mqa — H^3)-(NC$_5$D$_5$)] (32) which has the configuration shown. The related complex [PdCl(MeC$_6$H$_3$CH=NMe)(NC$_5$D$_5$)] (35) was prepared from 4-MeC$_6$H$_4$CH=NMe for comparison with (32) and the two were shown to be spectroscopically, and presumably structurally, related. By analogy with related palladation products, we believe that (28) is a chloro-bridged dimer which is then cleaved with pyridine. Interestingly its isomer, compound (25), does not show this characteristic cleavage with pyridine but only reacts
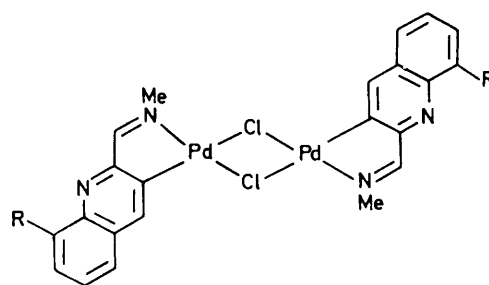
(28) R = Me

(30) R = Et

(31) R = Pr^i
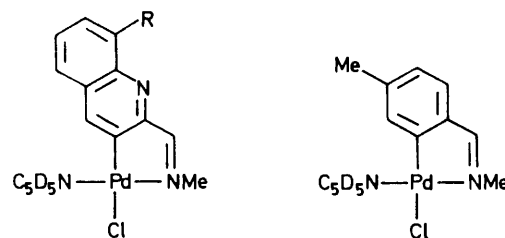
(32) R = Me   (35)

(33) R = Et

(34) R = Pr^i

with PEt$_3$ which is a better ligand. Consequently we believe that (25) does not contain chloro-bridges but rather mqa—H^8 is a tridentate ligand as shown and that PEt$_3$ displaces the imine end of the ligand since n.m.r. indicates this to be non-co-ordinated in complex (26).

The ligands eqa and iqa are only metallated at the 3-position even with palladium acetate which gave exclusive 8-Me metallation with mqa. Complexes (29), (30), (33), and (34) were prepared and characterised in a similar manner to that described for the mqa derivatives.

EXPERIMENTAL

Ligand Synthesis.—We have developed two routes to the imine ligands (Scheme 1), one *via* (8-methyl-2-quinolyl)-lithium, a method which may be modified to prepare a range of related 2-substituted quinolines, and the other *via* direct oxidation of 2,8-dimethylquinoline to the 2-formyl-8-methyl compound. The latter route is best used to prepare variously 8-substituted derivatives (*e.g.* 8-ethyl or 8-isopropyl compounds). 8-Methylquinoline (Koch–Light Ltd.), 2-methylaniline, 2-ethylaniline (Aldrich Ltd.), and 2-isopropylaniline (Fluka A.G.) were used as purchased.

Route 1. *2-Bromo-8-methylquinoline.* A mixture of dimethyl sulphate (60 cm^3) and 8-methylquinoline (30.0 g) was boiled for *ca.* 1 min to start an exothermic reaction. After this was over the mixture was allowed to cool to give a white solid mass which was extracted with water (4 × 50 cm^3). This aqueous solution was used for the next stage of the synthesis. [A pure sample of 8-methyl-*N*-methyl-quinolinium methyl sulphate as white crystals could be obtained by evaporation and recrystallisation of the white solid from aqueous ethanol (Found: C, 53.0; H, 5.65; N, 5.05. C$_{12}$H$_{15}$NO$_4$S requires C, 53.3; H, 5.55; N, 5.2%).] The aqueous solution was added to a solution of K$_3$[Fe(CN)$_6$] (120 g) in water (600 cm^3) to give immediately a yellow suspension. Addition of a considerable quantity of diethyl ether and an aqueous solution of K[OH] (500 cm^3, 10%) while stirring vigorously led to the extraction of dark yellow material into the ether layer. Successive ether extractions (using 3.0 dm^3 in all) allowed total extraction of the yellow material. A chloroform solution of the residual oil after removal of ether was dried over Mg[SO$_4$] and evaporated to give 1,8-dimethylquinolone as a yellow *solid* (32.4 g, 90%) (Found: C, 76.4; H, 6.5; N, 7.95. C$_{11}$H$_{11}$NO requires C, 76.3; H, 6.4; N, 8.1%).

A mixture of this yellow quinolone and freshly prepared PBr$_5$ (75 g) was heated to 100 °C for 1—2 h in a three-necked flask (250 cm^3) fitted with condenser and drying tube. Methyl bromide was evolved to give a yellow melt which was cooled to give a thick oil. After careful hydrolysis the oil–water mixture was neutralised with K[OH] and extracted with chloroform (4 × 50 cm^3), the extract being dried over Na$_2$[SO$_4$] and evaporated under reduced pressure to give the crude product as an off-white solid (38.0 g). Elution through a short silica column with CH$_2$Cl$_2$ removed the colouration and recrystallisation of the resulting white solid (boiling light petroleum, 100—120 °C) gave white *needles* (34.3 g, 82% from the quinolone, 74% overall), m.p. 77—78 °C (lit.,[11] 78—79 °C) (Found: C, 53.5; H, 3.75; Br, 36.1; N, 6.15. C$_{10}$H$_8$BrN requires C, 54.1; H, 3.65; Br, 36.0; N, 6.3%). 2,3,6-Tribromo-8-methyl-quinoline (0.71 g) was obtained as a by-product from the mother liquor by fractional recrystallisation (Found: C, 32.0; H, 1.65; Br, 63.3; N, 3.85. C$_{10}$H$_6$Br$_4$N requires C, 31.6; H, 1.6; Br, 63.1; N, 3.7%).

8-Methylquinoline-2-carboxaldehyde. A solution of 2-bromo-8-methylquinoline (5.0 g, 22.5 mmol) in diethyl ether (25 cm^3) was added to a freshly standardised solution of LiBu (25 mmol) in ether (30 cm^3) at −20 °C with vigorous stirring. After 5 min at room temperature, dimethyl-formamide (dmf) (2.0 cm^3) in ether (10 cm^3) was added to the cooled red solution (−30 to −40 °C) giving an immediate white precipitate. The mixture was hydrolysed with aqueous [NH$_4$]Cl at room temperature and extracted with ether. The red ether layer was dried over Na$_2$[SO$_4$], evaporated to dryness, and the residue recrystallised from

hot light petroleum to give the product as yellow crystals (2.44 g, 63%), m.p. 83—84 °C (lit.,[12] 83.5 °C) (Found: C, 76.7; H, 5.3; N, 8.1. C$_{11}$H$_9$NO requires C, 77.15; H, 5.3; N, 8.2%).

8-Methylquinoline-2-carboxaldehyde-N-methylimine (mqa). A solution of the aldehyde in benzene was treated with an ethanolic solution of methylamine (1.1 equivalent) and the mixture refluxed in an apparatus fitted with a Dean–Stark trap until no more water came over. Evaporation followed by recrystallisation of the residue from light petroleum gave the imine as colourless *crystals* (96%) (Found: C, 78.0; H, 6.55; N, 15.2. C$_{12}$H$_{12}$N$_2$ requires C, 78.25; H, 6.55; N, 15.2%).

Route 2. *2,8-Dimethylquinoline.* Concentrated HCl (360 cm^3) was carefully added to a cooled sample of 2-methyl-aniline (216 g) followed by paraldehyde (2,4,6-trimethyl-*s*-trioxan) (270 g) in a three-necked flask (2 dm^3) fitted with an efficient condenser. On warming up to room temperature an extremely vigorous exothermic reaction occurred and the mixture was refluxed for 3 h after this had subsided. After cooling, the mixture was neutralised and steam distilled. The first 500 cm^3 of distillate contained most of the volatile impurities, but later fractions contained almost pure product. Fractionation gave the pure product (65 g, 20.5%), b.p. 136 °C (18 mmHg).*

8-Methylquinoline-2-carboxaldehyde. Over 15 min, a solution of 2,8-dimethylquinoline (16.5 g) in dioxan (25 cm^3) was added to a solution of selenium dioxide (14.0 g) in dioxan (130 cm^3) and water (6 cm^3) at 45—50 °C. The resulting green mixture was refluxed for 1 h, the dioxan removed, and the oily solids steam distilled to give the product aldehyde (5.2 g, 29%).

By essentially the same procedure, 8-ethylquinoline-2-carboxaldehyde (64%) and 8-isopropylquinoline-2-carbox-aldehyde (40%) were synthesised from the appropriate substituted anilines.

The methylimines of these aldehydes were simply prepared as described above: 8-ethylquinoline-2-carboxalde-hyde-*N*-methylimine (eqa) (Found: C, 77.7; H, 7.3; N, 12.75. C$_{13}$H$_{14}$N$_2$ requires C, 78.75; H, 7.1; N, 14.15%) and 8-isopropylquinoline-2-carboxaldehyde-*N*-methylimine (iqa) (Found: C, 79.7; H, 7.6; N, 12.6. C$_{14}$H$_{16}$N$_2$ requires C, 79.2; H, 7.6; N, 13.2%).

Metal Complex Synthesis.—[RhCl(CO)$_2$(mqa)] (1). A solution of mqa (0.050 g) in light petroleum (b.p. 40—60 °C, 1.0 cm^3) was added to a solution of [Rh$_2$Cl$_2$(CO)$_4$] (0.050 g) in light petroleum (5.0 cm^3). A yellow *precipitate* formed immediately, and was filtered off, washed with light petroleum, and dried (0.082 g, 84%). The eqa and iqa complexes (2) and (3) were prepared similarly as yellow *precipitates.*

[RhCl(cod)(mqa)] (4). An excess of mqa (0.080 g) was added to a solution of [Rh$_2$Cl$_2$(cod)$_2$] (0.100 g; cod = cyclo-octa-1,5-diene) in chloroform (3 cm^3). Addition of light petroleum gave the product as a fine yellow *powder* (0.132 g, 76%).

[IrH(Cl)(mqa − H^3){P(C$_6$H$_{11}$)$_3$}$_2$] (5). Using a method based on that of Vrieze and co-workers,[3] with degassed solvents under N$_2$, a solution of tricyclohexylphosphine (0.652 g) in benzene (1 cm^3) was added slowly to a vigorously stirred mixture of mqa (0.236 g) and [Ir$_2$Cl$_2$(C$_8$H$_{14}$)$_4$] (C$_8$H$_{14}$ = cyclo-octene) (0.500 g) in benzene (20 cm^3). The resulting clear red solution was refluxed for 2 h and the solvent was removed from the cooled, filtered, red solution

* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

under vacuum. A red pentane extract (40 cm^3) of the residue was filtered and evaporated under vacuum to a red glass which gave deep red *crystals* (0.360 g, 36%) on dissolving in diethyl ether and cooling to -15 °C. The above purification, necessary to remove C_8H_{14}, leads to a yield lower than that actually formed.

The complex [RhH(Cl)(mqa $-$ H^3){P(C$_6$H$_{11}$)$_3$}$_2$] (6) was similarly isolated (0.370 g) as bright yellow *crystals* (from diethyl ether at -78 °C) using [Rh$_2$Cl$_2$(C$_8$H$_{14}$)$_4$] (0.400 g), P(C$_6$H$_{11}$)$_3$ (0.652 g), and mqa (0.236 g).

[PdCl$_2$(qa)] (7). A solution of qa (0.058 g) in methanol (1 cm^3) was added to a solution of Na$_2$[PdCl$_4$] (0.100 g) in methanol (5 cm^3). The red colour was immediately discharged and the product obtained as a yellow *precipitate* (0.098 g, 84%) which was washed with methanol and diethyl ether and is very sparingly soluble in organic solvents.

[PdCl$_2$(mqa)$_2$] (8). A solution of mqa (0.217 g) in methanol (1 cm^3) was added to a solution of Na$_2$[PdCl$_4$] (0.100 g) in methanol (5 cm^3). The red colour was discharged and a white *precipitate* (0.162 g, 86%) slowly formed over 30 min, was filtered off and washed with methanol and diethyl ether. The corresponding eqa (9) (82%) and iqa (10) (89%) complexes were prepared similarly as white *precipitates*.

[{PdCl$_2$(mqa)}$_n$] (11). A mixture of [PdCl$_2$(NCPh)$_2$] (0.100 g) and mqa (0.048 g) in chloroform was refluxed for 30 min, cooled, and the resulting orange precipitate (0.076 g, 80%) was washed with diethyl ether. This product was purified by Soxhlet extraction with CH$_2$Cl$_2$ which gave compound (11) as an orange *solid*, while traces of insoluble [PdCl$_2$(mqa)$_2$] (8) were not extracted.

[Pd(O$_2$CMe)$_2$(mqa)$_2$] (12). A solution of mqa (0.170 g) in dichloromethane (1 cm^3) was added to a solution of palladium(II) acetate [Pd$_3$(O$_2$CMe)$_6$] (0.100 g) in dichloromethane (20 cm^3) and the solvent rapidly removed under reduced pressure at sub-ambient temperatures. Addition of light petroleum to the residue gave the product as a pale yellow *solid* which was washed with ether and dried (0.235 g, 87%). Over a period of hours in solution, the formation of the 8-CH$_3$-metallated complex prevented the isolation of pure [Pd(O$_2$CMe)$_2$(mqa)$_2$].

[PdCl(dmp)(mqa)] (13). An excess of mqa (0.100 g) was added to a solution of [{PdCl(dmp)}$_2$] (0.100 g; dmp = 2-*NN*-dimethylaminoethylphenyl-*NC*) in chloroform (0.100 g). Addition of light petroleum gave the product as white *microcrystals* (0.140 g, 84%).

[Pd(NO$_3$)(dmp)(mqa)] (14). Silver(I) nitrate (0.062 g) in acetone (5 cm^3) was added to [{PdCl(dmp)}$_2$] (0.100 g). The AgCl formed was filtered off and an excess of mqa (0.100 g) was added to the filtrate. Addition of diethyl ether gave the product as white *needles* (0.139 g, 77%).

[PdCl(η-C$_3$H$_5$)(mqa)] (15). The ligand mqa (0.120 g, 1.1 mol per mol Pd) was added to a solution of [{PdCl-(η-C$_3$H$_5$)}$_2$] (0.100 g) in dichloromethane (2 cm^3). Removal of the solvent from the yellow solution under reduced pressure and addition of light petroleum gave the product as a lemon-yellow *solid* (0.120 g).

[Pd(η-C$_3$H$_5$)(mqa)][ClO$_4$] (17). Silver(I) perchlorate (0.118 g) in acetone (1 cm^3) was added to a solution of [{PdCl(η-C$_3$H$_5$)}$_2$] (0.100 g) in acetone (5 cm^3). Addition of mqa (0.120 g) and diethyl ether to the filtered solution gave yellow *crystals* which were recrystallised (87% yield) from dichloromethane–diethyl ether. The corresponding compounds (16), (18)—(20), (22), and (23) with mqa, eqa, or

iqa (Table 1) were prepared similarly with 70—90% yields of the pure yellow crystalline *products*. The corresponding qa complex [Pd(η-C$_3$H$_5$)(qa)][ClO$_4$] (21) (92% yield) is quite different, giving an almost totally insoluble colourless *precipitate* on addition of qa to the appropriate solution as above.

A similar preparation to that above, but with addition of a large excess of mqa (0.5 g) and adding diethyl ether to the concentrated solution, gave [Pd(η-C$_3$H$_5$)(mqa)$_2$][ClO$_4$] (24) as a white *precipitate*.

Palladation of mqa.—(1) *With* [PdCl$_4$]$^{2-}$. A solution of Na$_2$[PdCl$_4$] (0.75 g) and mqa (0.5 g) in methanol (60 cm^3) was refluxed for 20 h to give a yellow precipitate (0.38 g). Soxhlet extraction of the solid with CH$_2$Cl$_2$ gave the more soluble [PdCl(mqa $-$ H^8)] (25) (0.15 g) as an orange *solid* and the insoluble [{PdCl(mqa $-$ H^3)}$_2$] (28) (0.20 g) as yellow *solid*, while the deep red methanolic mother liquor gave after chromatography the dimethyl acetal of 8-methylquinoline-2-carboxaldehyde as a colourless oil (0.16 g) (Found: C, 71.7; H, 6.95; N, 6.4. C$_{13}$H$_{15}$NO$_2$ requires C, 71.85; H, 6.95; N, 6.45%) and a red solid (0.37 g) presumed to contain [PdCl$_4$]$^{2-}$.

Similar reactions with eqa or iqa gave compounds (30) (45%) and (31) (64%) as yellow solids.

(2) *With* [Pd$_3$(O$_2$CMe)$_6$]. A solution of palladium(II) acetate (1.0 g) and mqa (0.9 g) in chloroform (50 cm^3) was warmed at 40 °C for 1 h. The deep red solution was cooled and filtered to remove a little black deposit; the filtrate was evaporated to dryness, the residue dissolved in benzene, and complex (27) precipitated as deep red *crystals* (1.56 g, 95%) with diethyl ether. A similar reaction with eqa gave complex (29) as a yellow *powder* (67%), and while the iqa analogue [{Pd(O$_2$CMe)(iqa $-$ H^3)}$_2$] was shown in an n.m.r. study to be formed similarly it was not isolated.

(3) *With* [AsPh$_4$]$_2$[Pd$_2$Cl$_6$]. A solution of the tetraphenyl-arsonium salt (0.126 g) and mqa (0.040 g) in dichloromethane (1 cm^3) was added to a preparative t.l.c. (silica) plate. Repeated elution with CH$_2$Cl$_2$ gave two bands: a colourless one giving 8-methylquinoline-2-carboxaldehyde (0.020 g, 50%) and a yellow one giving complex (25) (0.032 g, 46%). Soluble derivatives of these metallated products were simply prepared and isolated as pale yellow *crystals* of compound (26) or as deep yellow *crystals* of compounds (32)—(34) in good yield.

X-*Ray Crystallography of* [Pd(η-C$_3$H$_5$)(iqa)][ClO$_4$].—Preliminary unit-cell parameters and the crystal system were determined from oscillation and Weissenberg photographs. The space group ($P2_1/c$) was uniquely determined from the systematic absences, $0k0$ for k odd and $h0l$ for l odd. The accurate cell parameters and the orientation matrix used for data collection were determined from least-squares refinement of the setting angles for 25 reflections ($14 < \theta < 18°$) automatically centred on an Enraf–Nonius CAD4 diffractometer.

Crystal data. C$_{17}$H$_{21}$ClN$_2$O$_4$Pd, $M = 459.2$, Monoclinic, $a = 8.598(1)$, $b = 8.142(1)$, $c = 27.400(3)$ Å, $\beta = 97.15(1)°$, $U = 1 903.3$ Å^3, space group $P2_1/c$ (C_{2h}^5, no. 14), $D_m = 1.59$ g cm^{-3}, $Z = 4$, $D_c = 1.60$ g cm^{-3}, $F(000) = 928$, λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 10.3 cm^{-1}.

Three-dimensional X-ray intensity data (h, k, $\pm l$; $1.5 < \theta < 25°$) were collected from a single crystal ($0.45 \times 0.13 \times 0.08$ mm) mounted on the CAD4 diffractometer using Mo-K_α radiation (graphite monochromator) and an ω—2θ scan technique. A periodic check of two standard reflections showed only minor fluctuations in their inten-

TABLE 7

Fractional co-ordinates (Pd $\times$ 10^5, others $\times$ 10^4) of the non-hydrogen atoms

Atom	x	y	z
Pd	79 989(3)	70 269(4)	40 446(1)
N(1)	7 166(4)	4 501(4)	3 943(1)
N(2)	8 062(4)	6 204(6)	4 765(1)
C(2)	6 564(5)	4 104(5)	4 350(2)
C(3)	5 364(6)	2 924(6)	4 360(2)
C(4)	4 726(6)	2 267(6)	3 935(2)
C(5)	4 787(6)	1 855(6)	3 051(2)
C(6)	5 518(7)	2 091(7)	2 651(2)
C(7)	6 900(6)	3 035(6)	2 679(2)
C(8)	7 538(5)	3 798(5)	3 106(2)
C(9)	6 686(5)	3 669(5)	3 514(2)
C(10)	5 356(5)	2 609(5)	3 494(2)
C(11)	7 198(6)	4 947(7)	4 794(2)
C(12)	8 739(9)	7 042(10)	5 218(3)
C(13)	9 181(6)	4 519(6)	3 170(2)
C(14)	334(6)	3 222(7)	3 402(2)
C(15)	9 706(9)	5 101(11)	2 685(3)
C(16)	8 386(8)	9 567(7)	4 125(3)
C(17)	8 549(10)	9 127(8)	3 644(3)
C(18)	7 432(9)	8 334(7)	3 363(3)
Cl	7 015(2)	2 796(2)	969(1)
O(1)	7 996(19)	1 463(14)	930(5)
O(2)	7 466(21)	3 918(24)	1 300(7)
O(3)	5 548(13)	2 354(17)	686(5)
O(4)	7 619(13)	4 048(15)	635(5)
O(5)	5 776(23)	3 196(21)	716(8)
O(6)	7 039(27)	3 448(26)	1 409(5)
O(7)	8 200(17)	2 023(35)	827(11)
O(8)	6 336(26)	1 467(30)	1 302(11)

sities. The data were corrected for the usual Lorentz and polarisation effects but no absorption corrections were made. Of 3 248 unique intensities, 2 437 were considered observed $[F_o > 3\sigma(F_o)]$ and used in the structure analysis and refinement.

The position of the palladium atom was determined from a three-dimensional Patterson synthesis, and the chlorine, nitrogen, and carbon atoms were located from successive difference-map calculations. Isotropic, full-matrix, least-squares refinement of these atoms reduced the R value to 0.12. The four oxygen atoms of the perchlorate group were found to be disordered and eight positions (each with a fixed occupancy of 0.5) were included in the refinement to obtain isotropic temperature factors of comparable magnitude. Further refinement with anisotropic temperature factors for all the non-hydrogen atoms reduced R to 0.058. Sixteen of the 21 hydrogen atoms were then located from difference maps, and isotropically refined with the C–H vector constrained at 1.08 Å. The allyl hydrogen atoms were not very clearly defined in the difference maps and these were ignored. The refinement finally converged at

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

$R = 0.041$ and R' $\{ = [\Sigma(w\Delta F^2)/\Sigma(wF_o^2)]^{\frac{1}{2}}\} = 0.044$. The weighting scheme $w = 1/[\sigma^2(F_o) + 0.000\ 4F_o^2]$ was used and this gave reasonably flat analyses of variance with sin θ, $(F_o/F_{max.})^{\frac{1}{2}}$, reflection indices, and parity groups. Fractional co-ordinates with their estimated standard deviations are given for non-hydrogen atoms in Table 7 and their derived interatomic distances and angles in Table 5. Selected least-squares planes and torsion angles are presented in Table 6. Thermal parameters, fractional co-ordinates of hydrogen atoms, and the observed and calculated structure factors are listed in Supplementary Publication No. SUP 22583 (15 pp.).* All calculations were performed on the ICL 1904S computer at Queen Mary College and the CDC 7600 computer at the University of London using the programs SHELX-76 [13] for structure solution and refinement, XANADU [14] for least-squares plane calculations, and PLUTO [15] for drawing the diagrams. Neutral-atom scattering factors were taken from refs. 16 (H) and 17 (Pd, Cl, O, N, and C), with those of the heavier elements being modified for anomalous dispersion, taking the $\Delta f'$ and $\Delta f''$ values from ref. 18.

REFERENCES

[1] A. J. Deeming, I. P. Rothwell, M. B. Hursthouse, and L. New, *J.C.S. Dalton*, 1978, 1490.
[2] A. J. Deeming and I. P. Rothwell, *J.C.S. Chem. Comm.*, 1978, 344.
[3] J. F. van Baar, K. Vrieze, and D. J. Stufkens, *J. Organometallic Chem.*, 1975, **97**, 461.
[4] S. E. Livingstone, *J. Proc. Roy. Soc. New South Wales*, 1951, **85**, 151; 1952, **86**, 32.
[5] D. N. Lawson and G. Wilkinson, *J. Chem. Soc. (A)*, 1965, 1900; W. Hieber, H. Heusinger, and O. Vohler, *Chem. Ber.*, 1957, **90**, 2425.
[6] B. L. Shaw and N. I. Tucker, ' Comprehensive Inorganic Chemistry,' Pergamon, Oxford, 1975, ch. 53.
[7] R. Mason and D. R. Russell, *Chem. Comm.*, 1966, 26.
[8] A. E. Smith, *Acta Cryst.*, 1969, **A25**, Suppl. S161.
[9] H. A. Graf, R. Hüttel, G. Nagarsen, and R. Bau, *J. Organometallic Chem.*, 1977, **136**, 389.
[10] G. A. Barclay, R. S. Vagg, and E. C. Watton, *Acta Cryst.*, 1978, **B34**, 1833.
[11] F. H. Case and J. J. Laffert, *J. Org. Chem.*, 1958, **23**, 1375.
[12] M. Seyhan, *Chem. Ber.*, 1957, **90**, 1386.
[13] G. M. Sheldrick, University of Cambridge.
[14] P. Roberts and G. M. Sheldrick, University of Cambridge.
[15] W. D. S. Motherwell, University of Cambridge.
[16] R. F. Stewart, C. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1956, **42**, 3175.
[17] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.
[18] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.