Rhodium(I) Complexes of 8-Methyl-, 8-Ethyl-, and 8-Isopropyl-quinolines and Related 2-Substituted Derivatives

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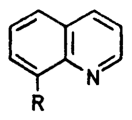
The complexes $[Rh(CO)(PPh_3)_2L][ClO_4]$ have been prepared from $[Rh(CO)(PPh_3)_2(CH_3COCH_3)][ClO_4]$ on adding unidentate L (8-methyl-, -ethyl-, or -isopropyl-quinoline) or bidentate L (1,10-phenanthroline or quinoline-2-carboxaldehyde-*N*-methylimine). 8-Alkyl-substitution of the latter ligand gives the complexes $[Rh(CO)(PPh_3)_2L][ClO_4]$ as isomers with uni- and bi-dentate L respectively with relative stabilities of the unidentate form depending on the 8-substituent in the order Pr^i > Et > Me. Unidentate L is also favoured by replacing PPh_3 by $P(C_6H_{11})_3$, but bidentate co-ordination is found using $AsPh_3$ or PMe_2Ph. Equilibrium constants for chloro-bridge cleavage of $[Rh_2Cl_2(CO)_4]$ by 8-substituted and 2,8-disubstituted quinolines are reduced by increasing the size of the 8-substituent and even more by further introduction of a 2-methyl group. The contributions of distortions in the co-ordination to these changes in equilibrium constants are discussed.

CO-ORDINATION through the nitrogen atom in 8-substituted quinolines requires that the 8-substituent be close to the metal atom. This has, of course, enabled the anion derived from 8-hydroxyquinoline to be used as a powerful bidentate ligand, while in the present work we have tried to establish the consequences of the 8-substituent being a Me, Et, or Pr^i group. Even though palladation of the 8-Me group of 8-methylquinoline readily occurs with $Na_2[PdCl_4]$ [1] or with palladium(II) acetate,[2] we have already shown that under suitable conditions unmetallated complexes of 8-methylquinoline and related ligands [3,4] may be prepared. An *X*-ray diffraction study of a closely related benzo[*h*]quinoline (bquin) complex has given a Pd $\cdots$ H(10) distance of 2.09 Å,[3] as short as any metal–hydrogen non-bonding interaction known. The use of bidentate ligands based on 8-substituted quinolines has also shown that the 8-substituent–metal interaction can dominate the nature of the complexes obtained.[5] In this paper we describe two closely related series of compounds, $[RhCl(CO)_2L]$ and $[Rh(CO)(PPh_3)_2L][ClO_4]$, where L is a ligand based on quinoline. By variously substituting the 2- and the 8-positions of quinoline we have established some of the factors affecting the stability of the carbonyl complexes with respect to ligand dissociation and formation of $[\{RhCl(CO)_2\}_2]$ and for the PPh_3 complexes we have shown that steric interactions are extremely important in determining whether potentially bidentate ligands achieve this mode of co-ordination.

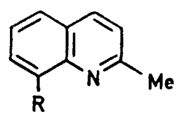
RESULTS AND DISCUSSION

The ligands used in this work and their abbreviations are shown below and the syntheses of those that are new are described in the Experimental section. The two series of rhodium(I) complexes will be described separately.

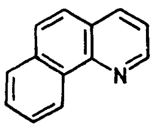
Complexes $[Rh(CO)(PPh_3)_2L][ClO_4]$.—It has been shown that when chloride is displaced from $[RhCl(PPh_3)_3]$ in the absence of other co-ordinating ions or molecules the cation $[Rh(PPh_3)_3]^+$ is formed in which a phenyl group of one PPh_3 ligand occupies the vacant co-ordination site.[6] In the presence of co-ordinating solvents the site is occupied by a solvent molecule. Similarly, treatment of $[RhCl(CO)(PPh_3)_2]$ with $Ag[ClO_4]$ in acetone leads to $[Rh(CO)(PPh_3)_2(CH_3COCH_3)][ClO_4]$ which may be isolated as yellow needles.[7] The $AsPh_3$ analogue was isolated similarly but the PMe_2Ph and $P(C_6H_{11})_3$ complexes were only obtained as oils. For each acetone-co-ordinated complex, ν(CO) for the carbonyl ligand occurs *ca.* 40 cm^{-1} to higher wavenumbers than for the neutral precursor although the



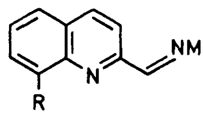
R = H (quin)
R = Me (8Me-quin)
R = Et (8Et-quin)
R = Pr^i (8Pr^i-quin)



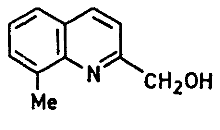
R = H (2Me-quin)
R = Me (2,8Me_2-quin)
R = Et (2Me,8Et-quin)
R = Pr^i (2Me,8Pr^i-quin)



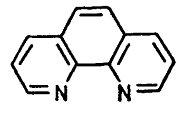
bquin



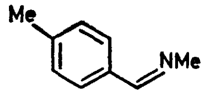
R = H (qa)
R = Me (mqa)
R = Et (eqa)
R = Pr^i (iqa)



2CH_2OH,8Me-quin



phen



4Me-ba

absolute values of ν(CO) are lower for the more basic phosphines.

These acetone complexes are useful precursors for substituted quinoline complexes; for example, various complexes $[Rh(CO)(PPh_3)_2L][ClO_4]$ (Table 1) were obtained by acetone displacement. All the nitrogen ligands used as indicated in Table 1 displaced acetone to give solutions with simple ν(CO) spectra around 2 000 cm^{-1}. A good number of these were isolated, fully characterised, and analysed. Those for which no analytical data are given were either not isolated or gave oils, so that the formulations of these are less reliable. Nevertheless all gave excellent quality i.r. and n.m.r. spectra and good correlations could be made between those fully characterised and those only observed in solution.

TABLE 1

Infrared and analytical data for complexes $[Rh(CO)L'_2L][ClO_4]$ where L′ is PPh_3, $AsPh_3$, PMe_2Ph, or $P(C_6H_{11})_3$ and L is a nitrogen-donor ligand or acetone. Solvent is CH_2Cl_2 unless indicated otherwise

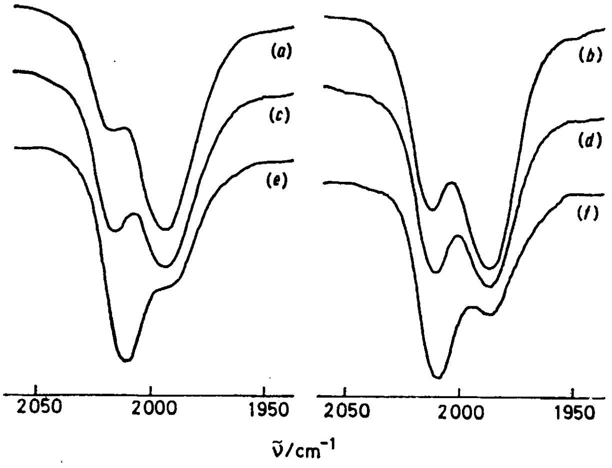
			Δ[ν(CO)] [b]/cm^{-1}		Analysis (%) [c]				
L′	L	ν(CO) [a]/cm^{-1}	Unidentate L	Bidentate L	C	H	N	Cl	P
PPh_3	$(CH_3)_2CO$	2 006			58.8 (59.1)	4.65 (4.45)	0 (0)	4.40 (4.35)	7.80 (7.60)
d	$(CH_3)_2CO$	2 006							
	mqa	2 011 (5.4), 1 988 (10)	+5	−18	56.95 (56.75) [e]	4.20 (4.10)	2.60 (2.65)	13.05 (13.4)	6.15 (5.90)
d	mqa	2 010 (7.6), 1 985 (10)	+4	−21					
	eqa	2 011 (8.2), 1 989 (10)	+5	−17	56.45 (57.1) [e]	4.20 (4.25)	2.55 (2.60)	13.95 (13.2)	5.95 (5.75)
d	eqa	2 010 (9.2), 1 986 (10)	+4	−20					
	iqa	2 012 (10), 1 994 (6.6)	+6	−12	56.95 (57.4) [e]	4.35 (4.35)	2.70 (2.60)	13.25 (13.05)	6.05 (5.70)
d	iqa	2 010 (10), 1 988 (6.5)	+4	−18					
	8Me-quin	2 006	0		62.75 (62.85)	4.30 (4.40)	1.40 (1.55)	4.10 (3.95)	7.05 (6.90)
	8Et-quin	2 005	−1		63.25 (63.2)	4.45 (4.55)	1.50 (1.55)	4.15 (3.90)	7.15 (6.80)
	8Pr^{i}-quin	2 006	0		63.5 (63.55)	4.75 (4.70)	1.55 (1.50)	3.75 (3.85)	6.85 (6.70)
	bquin	2 007	+1		53.2 (53.25) [f]	3.50 (3.50)	1.30 (1.20)	19.9 (21.15)	5.65 (5.30)
	4Me-ba	2 010	+5						
	qa	1 946		−60	51.6 (51.6) [f]	3.65 (3.65)	2.30 (2.40)	20.95 (21.3)	5.55 (5.30)
	phen	1 944		−62	62.6 (62.95)	4.15 (4.10)	3.50 (3.00)	3.95 (3.80)	6.25 (6.60)
$AsPh_3$	$(CH_3)_2CO$	2 002	0		53.3 (53.35)	4.50 (4.05)	0 (0)	3.80 (3.95)	
	mqa	1 985		−17	52.4 (52.4) [e]	3.95 (3.80)	2.55 (2.45)	11.0 (12.35)	
	eqa	1 985		−17					
	iqa	2 008 (2.5), 1 985 (10)	+2	−17	52.9 (53.2) [e]	4.10 (4.10)	2.25 (2.4)	12.4 (12.05)	
	4Me-ba	2 009	+7						
PMe_2Ph	$(CH_3)_2CO$	1 994	0						
	mqa	1 979		−15					
	eqa	1 980		−14					
	iqa	2 000 (<1), 1 982 (10)	+6	−12					
	4Me-ba	1 999	+5						
$P(C_6H_{11})_3$	$(CH_3)_2CO$	1 977	0						
	mqa	1 982	+5						
	eqa	1 982	+5						
	iqa	1 982	+5						
	4Me-ba	1 983	+6						

[a] Relative intensities are given in parentheses. [b] Δ[ν(CO)] = [ν(CO)(L = *N*-donor ligand) − ν(CO) (L = acetone)]. [c] Calculated figures are given in parentheses. Compounds for which analytical data were not obtained were prepared in solution by addition of the appropriate ligand to the acetone complexes, but were not isolated. [d] Solvent is $(CH_3)_2CO$. [e] Formulated as $[Rh(CO)L'_2L][ClO_4]\cdot CHCl_3$. [f] Formulated as $[Rh(CO)L'_2L][ClO_4]\cdot 2CHCl_3$.

Unidentate ligands each gave a single isomeric product with a single symmetrical ν(CO) absorption close to that of the acetone complex and within the range 2 005—2 012 cm^{-1}. Either an imine nitrogen atom (for 4Me-ba) or a quinoline nitrogen atom (for 8Me-, 8Et-, or 8Pr^{i}-quin, or bquin) is co-ordinated and we take ν(CO) in this range to be characteristic of unidentate co-ordination. With other phosphines or arsines different wavenumber ranges were relevant, but in each case Δ[ν(CO)] values, defined as [ν(CO)(L = nitrogen-based ligand) —ν(CO)

(L = acetone)], in the range −1 to +7 cm^{-1} are found for unidentate co-ordination.

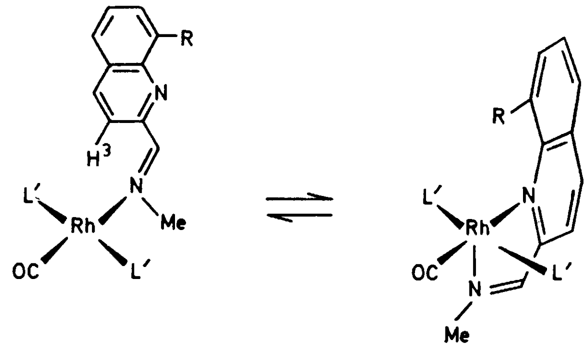
This knowledge was used when corresponding complexes [Rh(CO)$(PPh_3)_2$L][ClO_4] where L is a good bidentate (phen or qa) or a possible bidentate (mqa, eqa, or iqa) were examined. 1,10-Phenanthroline (phen) and qa give related five-co-ordinate complexes with Δ[ν(CO)] −62 and −60 cm^{-1} respectively; the build-up of negative charge at the metal atom relative to the situation where unidentate ligands are used may account for these large negative values. Proton n.m.r. spectra confirmed bidentate co-ordination. There is no evidence for loss of PPh_3 from these complexes to give square-planar complexes with bidentate L. Although there is no special significance in the above results, very different behaviour is found when the 8-position of qa is substituted by alkyl groups and with mqa, eqa, and iqa rapidly interconverting four- and five-co-ordinate isomers are observed. The Figure shows ν(CO) spectra for [Rh(CO)$(PPh_3)_2$L][ClO_4] where L = mqa, eqa, or iqa in CH_2Cl_2 or acetone solution. In each case two ν(CO) absorptions are observed, one with a Δ[ν(CO)] range of 4—6 cm^{-1}, the other with a range of −12 to −21 cm^{-1} and we ascribe these to isomers (A) and (B) with uni- and bi-dentate co-ordination respectively. With L = 4-methylbenzaldehyde-*N*-methylimine (4Meba), Δ[ν(CO)] = 5 cm^{-1}, very close to the lower wavenumber absorption for the mqa, eqa, and iqa isomers (A).



ν(CO) spectra for complexes [Rh(CO)$(PPh_3)_2$L][ClO_4]. L = mqa in CH_2Cl_2 (*a*) and CH_3COCH_3 (*b*), eqa in CH_2Cl_2 (*c*) and CH_3COCH_3 (*d*), and iqa in CH_2Cl_2 (*e*) and CH_3COCH_3 (*f*)

ν(CO) for isomers (B) depends rather more on the nature of the 8-substituent as might be expected for bidentate co-ordination. As can be seen in the Figure, the proportion of isomer (B) decreases in the order mqa > eqa > iqa as expected for increasingly unfavourable interactions between the 8-substituent and the metal atom. Isomers (A) and (B) are in rapid equilibrium since ^{1}H n.m.r. spectra in all cases show only single sets of averaged resonances. Close Rh to H contacts in the sixth site of these five-co-ordinate species are destabilising as are such interactions in a fifth 'axial' site of square-planar d^8 complexes. The greater favourability of isomer (A) when L = iqa compared with L = mqa or eqa is apparent from colour differences as well as from ν(CO) spectra (Figure). Isomers (A) are yellow but (B) red. Thus solutions of [Rh(CO)$(PPh_3)_2$(iqa)][ClO_4] are orange [predominantly (A)] but deposit pale yellow crystals [totally (A)], whereas both crystals [totally (B)] and solutions [predominantly (B)] of the mqa and eqa complexes are deep red.

The ^{1}H n.m.r. spectra of complexes [Rh(CO)$(PPh_3)_2$L][ClO_4] (L = mqa, eqa, or iqa), even at the lowest temperatures recorded (−60 °C), are time-averaged over isomers (A) and (B), but for L = iqa we observed a shift in the equilibrium from isomer (A) towards (B) at reduced temperatures (Table 2). For isomer (B) (as judged by the complexes where L = mqa or eqa where this predominates) the H^3 signal is at an anomalously high field and obscured by other signals in the region δ 7.1—7.6. This is attributed to shielding effects of the phenyl rings of the *cis*-PPh_3 ligands. In contrast, the H^3 signal for [Rh(CO)$(PPh_3)_2$(iqa)][ClO_4] is isochronous at 20 °C with the H^4 signal, giving a combined singlet at δ 8.12. In isomer (A) the H^3 signal is shifted downfield as a result of paramagnetic anisotropic effects of the square-planar geometry of rhodium and this more than compensates for any upfield shift due to neighbouring phenyl groups. As the spectrum of [Rh(CO)$(PPh_3)_2$(iqa)][ClO_4] is recorded at increasingly lower temperatures, the H^3 signal moves upfield as the contribution made by isomer (B) increases: the H^4 signal does not shift with temperature. At −60 °C the spectrum in the range δ 7—9 is similar to those for L = mqa or eqa. Similarly, as the temperature is lowered the C*H*$(CH_3)_2$ signal is shifted downfield with an increased influence of the paramagnetic anisotropy (deshielding effect) as this hydrogen atom spends more time close to the rhodium atom as the contribution from isomer (B) increases.



(A) (B)

Isomers in equilibrium. L′ = PPh_3, $AsPh_3$, PMe_2Ph, or $P(C_6H_{11})_3$

The proportions of isomers (A) and (B) are changed considerably on replacing PPh_3 in [Rh(CO)$(PPh_3)_2$L][ClO_4] (L = mqa, eqa, or iqa) by $AsPh_3$ or other tertiary phosphines, with isomer (B) being favoured as steric crowding at rhodium is reduced. The ligands PMe_2Ph and $P(C_6H_{11})_3$ are both more basic than PPh_3 with ν(CO) for the complexes $[Rh(CO)L'_2(CH_3COCH_3)][ClO_4]$ occurring 12 and 27 cm^{-1} respectively lower than for L = PPh_3. It must be for steric reasons therefore that replacement of PPh_3 (Tolman's cone angle of 145°) by PMe_2Ph (cone angle 122°) leads exclusively to isomers (B), except for a trace of isomer (A) when the 8-substituent is as large as Pr^i. Only isomers (A) are obtained where L = $P(C_6H_{11})_3$ (cone angle 170°) (see Table 1). The $AsPh_3$ complexes also form isomers (B) predominantly; longer Rh–As and As–C bonds give less sterically crowded complexes. The complex $[Rh(CO)(AsPh_3)_2(iqa)][ClO_4]$ gives red crystals, in contrast with the yellow crystals of the corresponding PPh_3 salt, consistent with their different structures

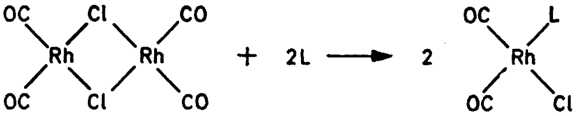
TABLE 2

Proton n.m.r. data for complexes $[Rh(CO)(EPh_3)_2L][ClO_4]$ (E = P or As) [a]

E	L	Solvent	Chemical shifts (δ)					
			H^2	H^4	H^3	8-R	NCH$_3$ [b]	Others
P	8Me-quin	CDCl$_3$	8.96 (dd)	7.91 (dd)	6.81 (dd)	3.39 (s)		6.9—7.6
	8Et-quin	CDCl$_3$	8.95 (dd)	7.93 (dd)	6.78 (dd)	4.17 (q), 1.14 (t)		6.9—7.6
	8Pr^i-quin	CDCl$_3$	8.99 (dd)	7.89 (dd)	6.83 (dd)	5.88 (m), 0.97 (d)		6.9—7.6
	bquin	CD$_2$Cl$_2$	9.05 (dd)	7.91 (dd)	6.98 (dd)			6.9—7.6; H^{10}, 11.18 (m)
	qa	CDCl$_3$		8.15 (d)	7.08 (d)	9.00 (m)	3.34 (s)	7.1—7.7
	mqa	CDCl$_3$		8.10 (d)	*c*	2.75 (s)	3.16 (s)	7.1—7.7
	eqa	CD$_2$Cl$_2$		8.14 (d)	*c*	3.60 (q), 1.00 (t)	3.04 (s)	7.1—7.7
	iqa	CDCl$_3$ [d]		8.12 (s)	8.12 (s)	4.88 (sp), 1.04 (d)	3.04 (s)	7.1—7.7
	iqa	CDCl$_3$ [e]		8.15 (d)	*c*	5.30 (m), 1.00 (d)	3.10 (s)	7.1—7.7
	4Me-ba	CDCl$_3$		8.20 (d)			2.86 (s)	7.1—7.7; 4Me, 2.32 (s)
	phen	CD$_2$Cl$_2$ [f]	9.12 (dd)	8.16 (dd)				7.0—7.8
As	mqa	CDCl$_3$		8.08 (d)		2.89 (s)	3.20 (s)	6.9—7.7
	iqa	CD$_2$Cl$_2$		8.08 (d)		5.35 (m), 0.97 (d)	3.15 (s)	

[a] Recorded on a Varian HA100 spectrometer at 27 °C unless stated otherwise. [b] Singlets slightly broadened due to coupling to MeN=C*H*. [c] Expected doublet upfield of δ 7.1 and obscured by other signals. [d] Recorded at 20 °C. [e] Recorded at −60 °C. [f] Recorded at 20 °C but the phen ligand still appears symmetrical at −85 °C.

Complexes $[RhCl(CO)_2L]$.—Chloro-bridge cleavage of $[Rh_2Cl_2(CO)_4]$ is an easy route to a range of complexes of type *cis*-$[RhCl(CO)_2L]$ [reaction (1)]; $[RhCl(CO)_2(py)]$ (py = pyridine) was originally prepared by this route.[8] No CO is displaced by amine ligands as in corresponding reactions with tertiary phosphines or isocyanides.[9,10] Measured equilibrium constants *K* for reaction (1) were used to assess the co-ordinating properties of a range of 8- and 2,8-substituted quinolines (see Experimental section for method of measuring *K*). For L = mqa, eqa, or iqa, the complexes $[RhCl(CO)_2L]$ have been described [5] and, since these are less crowded than the PPh_3 complexes above, only five-co-ordinate complexes corresponding with isomer (B) are formed. The values of *K* in these cases were too large to be measured in the same way as the values given in Table 3. For the unidentate ligands given in Table 3, reaction (1) is a rapid equilibrium and ^1H n.m.r. spectra at 27 °C show only broad averaged signals for the co-ordinated and free ligands. Indeed in order to use ^1H n.m.r. spectra to determine *K*, low temperatures (−25 °C) were required to obtain separate signals which could be integrated.



(1)

TABLE 3

Infrared data for complexes *cis*-$[RhCl(CO)_2L]$ in cyclohexane and equilibrium constants for reaction (1) at −25.0 ± 0.5 °C measured in CDCl$_3$

L	ν(CO)/cm^{-1}	*K*/dm^3 mol^{-1}
8Me-quin	2 009, 2 084	55 000 ± 10 000
8Et-quin	2 010, 2 086	2 700 ± 300
8Pr^i-quin	2 009, 2 085	480 ± 50
bquin	2 008, 2 085	*a*
2,8Me$_2$-quin	2 009, 2 085	90 ± 10
2Me,8Et-quin	2 008, 2 086	15 ± 2
2Me,8Pr^i-quin	2 007, 2 085	0.8 ± 0.1
2Me-quin	2 008, 2 084	*b*
2CH$_2$OH,8Me-quin	2 008, 2 086	2.3 [c] ± 0.2

[a] Too small to measure easily. [b] Too large to measure easily. [c] Measured at −45.0 ± 0.5 °C.

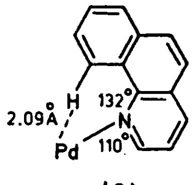
Since the values of ν(CO) (Table 3) are almost independent of the 2- and 8-substituents, we believe that variations of *K* are largely due to steric effects. With the 8-substituted ligands, 8Me-, 8Et-, and 8Pr^i-quin, there is a steady decrease in *K* on increasing the size of the 8-substituent and a similar variation of *K* with varying size of the 8-substituent is also found when the ligand is additionally 2Me-substituted. For the 2,8-substituted quinolines the absolute values of K are lower than for the 8-substituted ones with the 2Me-substituent reducing K by a factor of *ca.* 200—600, which is a larger effect than changing the 8-substituent from Me to Et or from Et to Pr^i. In a similar chloro-bridge-splitting reaction with palladium(II) there was essentially no change in K on going from py to 2Me-py [3] and the very large effect of the 2-substituent in this case is because the 8-substituent and the metal atom are already considerably compressed. For a bquin palladium complex, $[Pd(C_6H_4CH_2NMe_2)(OH_2)(bquin)][ClO_4]$, we have shown that there is a tilt as in (C) and similar tilts are to be expected in 8-substituted quin complexes. We conclude that the ability to relieve metal–8-substituent repulsions in this way is adversely affected by introducing a 2-methyl group.

TABLE 4

Proton n.m.r. and analytical data for complexes $[RhCl(CO)_2L]$ and free ligands L

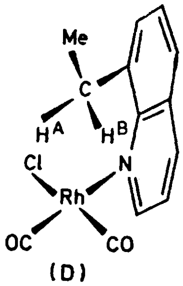
		Chemical shift [a]				Analysis (%) [b]			
Compound	L	2-substituent	H^4	Other ring protons	8-substituent	C	H	N	Cl
Free ligand	2,8Me$_2$-quin	2.71 (s, CH$_3$)	7.90 (d)	7.0—7.7	2.79 (s, CH$_3$)				
	2Me,8Et-quin	2.70 (s, CH$_3$)	7.89 (d)	7.0—7.7	3.34 (q, CH$_2$), 1.36 (t, CH$_3$)				
	2Me,8Pr^i-quin	2.71 (s, CH$_3$)	7.88 (d)	7.0—7.7	4.40 (sp, CH), 1.36 (d, CH$_3$)				
	2Me-quin	2.70 (s, CH$_3$)	7.92 (d)	7.0—7.8	8.10 (m, H)				
	2CH$_2$OH,8Me-quin	4.90 (s, CH$_2$)	8.07 (d)	7.1—7.8	2.78 (s, CH$_3$)				
[RhCl(CO)$_2$L] complexes	8Me-quin	9.53 (m, H)	8.38 (dd)	7.2—7.9	3.63 (s, CH$_3$)	42.45 (42.7)	2.70 (2.7)	4.15 (4.15)	10.5 (10.5)
	8Et-quin	9.55 (m, H)	8.37 (m)	7.2—7.9	4.21 (sx, CH$_2$), 4.61 (sx, CH$_2$), 1.45 (t, CH$_3$)	44.25 (44.4)	3.15 (3.15)	3.95 (4.0)	10.2 (10.1)
	8Pr^i-quin	9.59 (m, H)	8.38 (m)	7.2—7.9	6.39 (br sp, CH); 1.40 (d, CH$_3$), 1.49 (d, CH$_3$)	46.0 (46.0)	3.70 (3.60)	3.90 (3.85)	9.50 (9.70)
	bquin [c]	9.54 (H)	8.34 (m)	7.5—8.1		47.25 (48.2)	2.60 (2.45)	3.60 (3.75)	10.4 (9.50)
	2,8Me$_2$-quin	3.50 (s, CH$_3$)	8.19 (m)	7.0—7.7	3.76 (s, CH$_3$)				
	2Me,8Et-quin	3.48 (s, CH$_3$)	8.13 (m)	7.0—7.8	4.21 (sx, CH$_2$), 4.91 (sx, CH$_2$) *d* (CH$_3$)				
	2Me,8Pr^i-quin	3.56 (s, CH$_3$)	8.19 (d)	7.0—7.8	6.68 (b, CH), 1.40 (d, CH$_3$), 1.51 (d, CH$_3$)				
	2CH$_2$OH,8Me-quin	5.68 (s, CH$_2$)	8.28 (m)	7.0—7.7	3.41 (s, CH$_3$)				
	2Me-quin	3.10 (s, CH$_3$)	8.19 (d)	7.1—7.9	9.02 (m, H)	43.0 (42.7)	2.80 (2.70)	4.15 (4.15)	10.7 (10.5)

[a] Measured in CDCl$_3$ at 27 °C (free ligands) and at −25 °C (complexes) on a Varian HA100 spectrometer; s = singlet; d = doublet; t = triplet; q = quartet; sx = sextet; sp = septet; br = broad; m = multiplet. [b] Calculated values are given in parentheses. [c] H^{10} at δ 11.05 (m). [d] Not recorded.



(C)

The ^{1}H n.m.r. spectra of the complexes $[RhCl(CO)_2L]$ (Table 4) are as expected with large downfield shifts on co-ordination for those hydrogen atoms approaching the Rh atom from above the co-ordination plane. The order of downfield shifts on co-ordination for geometrically related hydrogen atoms is 8-Me$_2$C*H*-quin > H^{10}-(bquin) > 8-MeC*H*$_2$-quin > 8-C*H*$_3$-quin; the greater shifts are associated with protons spending more time closer to the rhodium atoms. Thus the Me$_2$C*H* proton is fixed conformationally close to the rhodium whereas the increased conformational flexibilities for the Et- and Me-substituted ligands mean that the shifts are averaged over different conformations, with a particular proton only experiencing a large downfield shift in perhaps one of these. Chiral configurations as in (D) for $[RhCl(CO)_2(8Et\text{-}quin)]$ are also found with 8Pr^i-quin, 2Me,8Et-quin, and 2Me,8Pr^i-quin. Thus the C*H*$_2$CH$_3$ signals in $[RhCl(CO)_2L]$ (L = 8Et-quin or 2Me,8Et-quin) appear as a pair of sextets, due to four-line coincidences in a 1 : 3 : 3 : 1 quartet of AB quartets. The



(D)

non-equivalences of the CH_2CH_3 and $CH(CH_3)_2$ protons in these complexes indicate that the molecules are chiral and that the bulk of the ligand remains on one side of the co-ordination plane and does not rapidly (at −25 °C) interchange between the two sides of the co-ordination plane which would result in site exchange of the protons. This does occur at higher temperatures by reaction (1) but not by rotation about the Rh–N bond. Whereas various conformations resulting from rotation about the 8Et–C bond are possible, that shown in (D) most likely predominates. Whatever conformations occur, on an average H^B will occupy a site above CO and H^A above Cl. The chemical-shift separation between the H^A and H^B signals is 0.40 p.p.m. (L = 8Et-quin) and 0.70 p.p.m. (L = 2Me,8Et-quin); H^B is in a deshielded region with respect to the anisotropic CO group and hence its signal is further downfield than that of H^A.

EXPERIMENTAL

Ligand Syntheses.—8-Methylquinoline (Koch-Light) and benzo[*h*]quinoline (Aldrich) were obtained commercially. 8-Ethyl- and 8-isopropyl-quinoline were synthesised by Skraup syntheses from 2-ethyl- and 2-isopropyl-aniline respectively using As_2O_5 as oxidant. The ligands 2Me-quin, $2,8Me_2$-quin, 2Me,8Et-quin, and $2Me,8Pr^i$-quin were similarly prepared from the appropriate 2-substituted anilines using acetaldehyde instead of glycerol in the Skraup synthesis. The compound $2CH_2OH,8Me$-quin was synthesised by adding a suspension of sodium tetrahydroborate (0.2 g) in isopropyl alcohol (20 cm^3) to a solution of 8-methylquinoline-2-carboxyaldehyde[5] (0.5 g) in diethyl ether (2 cm^3). After 10 min, water was added and the product (0.48 g, 96%) was extracted with chloroform and obtained as colourless crystals (Found: C, 75.85; H, 6.4; N, 7.95. $C_{11}H_{11}NO$ requires C, 76.25; H, 6.4; N, 8.1%). The syntheses of qa, mqa, eqa, and iqa have been described.[5]

Complex Syntheses.—$[Rh(CO)(PPh_3)_2(CH_3COCH_3)][ClO_4]$. Silver perchlorate (0.6 g) in acetone solution (5 cm^3) was added to a suspension of $[RhCl(CO)(PPh_3)_2]$ (2.0 g) in acetone (20 cm^3). The mixture was stirred for 5 min and the solvent was removed from the deep yellow solution, after the AgCl had been filtered off, until the volume had been reduced to 10 cm^3. Addition of diethyl ether gave the product as fine yellow *needles* (2.16 g, 93%). The salt $[Rh(CO)(AsPh_3)_2(CH_3COCH_3)][ClO_4]$ was obtained similarly as chunky orange-yellow *crystals* (87%), but the corresponding $P(C_6H_{11})_3$ and PMe_2Ph complexes were only obtained as oils. Infrared spectra of these oils were recorded in CH_2Cl_2 but they were not obtained analytically pure.

$[Rh(CO)(PPh_3)_2(8Me\text{-}quin)][ClO_4]$ *and related salts.* 8Me-quin (0.1 g, 1.4 mol per mol Rh) in chloroform (5 cm^3) was added to a solution of $[Rh(CO)(PPh_3)_2(CH_3COCH_3)][ClO_4]$ (0.41 g). Addition of diethyl ether gave the product as yellow *needles* (0.39 g, 87%). Sometimes small amounts of $CHCl_3$ were occluded in these crystals but could be removed by extended vacuum treatment. The corresponding complexes of 8Et-quin, $8Pr^i$-quin, and 4Me-ba were obtained similarly and in similar yields. Using bquin it was found unnecessary to add diethyl ether as the product crystallised from chloroform as pale yellow needles of $[Rh(CO)(PPh_3)_2(bquin)][ClO_4]\cdot 2CHCl_3$.

$[Rh(CO)(PPh_3)_2(qa)][ClO_4]\cdot 2CHCl_3$. Addition of qa (0.050 g, 1.25 mol per mol Rh) to a solution of $[Rh(CO)(PPh_3)_2(CH_3COCH_3)][ClO_4]$ (0.2 g) in chloroform (5 cm^3) gave the product as white *needles* (0.15 g, 50%). A similar treatment with 1,10-phenanthroline gave orange-yellow *microcrystals* of $[Rh(CO)(PPh_3)_2(phen)][ClO_4]$ (76%) which did not contain occluded solvent molecules.

$[Rh(CO)(PPh_3)_2(mqa)][ClO_4]\cdot CHCl_3$. Mqa (0.050 g, 1.1 mol per mol Rh) was added to a solution of $[Rh(CO)(PPh_3)_2(CH_3COCH_3)][ClO_4]$ (0.2 g) in chloroform (5 cm^3). Careful addition of diethyl ether to the red solution gave the product as deep red *crystals* (0.175 g, 66%). Eqa gave a similar deep red crystalline product, but in contrast a similar treatment with iqa gave the product $[Rh(CO)(PPh_3)_2(iqa)][ClO_4]\cdot CHCl_3$ as pale yellow *crystals* from an orange solution.

$[RhCl(CO)_2(8Me\text{-}quin)]$. An excess of 8Me-quin (0.5 g) was added to a solution of $[\{RhCl(CO)_2\}_2]$ (0.4 g) in light petroleum (b.p. 40—60 °C, 20 cm^3) and the solution was cooled to −15 °C to give the product as white *crystals* (0.55 g, 80%). Similar yields of the 8Et-quin, $8Pr^i$-quin, and 2Me-quin complexes were obtained in the same way, all as white *crystals*, but a similar treatment with bquin gave $[RhCl(CO)_2(bquin)]$ (48%) as a grey solid for which recrystallisation was impossible due to instability.

Equilibrium-constant Measurements.—Equilibrium constants for reaction (1) were measured in $CDCl_3$ solution at −25 ± 0.5 °C. In the cases of 8Me-quin, 8Et-quin, and $8Pr^i$-quin, samples of the complexes $[RhCl(CO)_2L]$ were weighed into an n.m.r. tube and solvent added to give a pre-calibrated volume of solution. At −25 °C separate signals were observed for free and co-ordinated ligand L which were integrated against each other. Hence the concentrations of L (*a*), $[RhCl(CO)_2L]$ (*b*), and of $[Rh_2Cl_2(CO)_4]$ (*c*) could be calculated and used in the expression $K = b^2/a^2c$. Adequately consistent values were obtained at different concentrations, confirming the validity of the expression. For other complexes it was better to weigh $[Rh_2Cl_2(CO)_4]$ and L into the n.m.r. tube in approximately equimolar quantities and to make up the solutions as before. Because of the difficulty in accurately preparing such concentrated solutions, there are large errors as indicated in Table 3, but nonetheless the trends as discussed are quite valid.

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