Journal of Organometallic Chemistry, 205 (1981) 117—131
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

PALLADATION BEHAVIOUR OF 8-METHYL-, 8-ETHYL-, AND 8-ISOPROPYL-QUINOLINES AND SOME OF THEIR 2-SUBSTITUTED DERIVATIVES

ANTONY J. DEEMING and IAN P. ROTHWELL

Department of Chemistry, University of College London, 20 Gordon Street, London WC1H 0AJ (Great Britain)

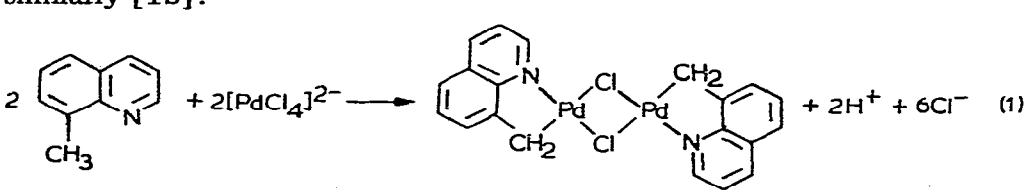
(Received July 18th, 1980)

Summary

8-Methyl- and 8-ethyl-quinolines give cyclopalladation products with palladium acetate by C—H bond cleavage at the 8-substituent, but 8-isopropylquinoline does not. The influence on cyclometallation of introducing 2-substituents (Me, Br, CHO, CH=NMe, CH_2OH, CO_2H) in these quinolines is described. The first three substituents totally prevent cyclopalladation whereas metallation at the 8-substituent proceeds smoothly when the 2-substituent is CH=NMe, CH_2-OH or CO_2H. The products are characterised spectroscopically and there is a discussion of the dynamic ^1H NMR behaviour of the *cis* and *trans* isomers of $[Pd(OAc)(CH_2C_9H_6N]_2$ formed from 8-methylquinoline. Evidence is presented that the cyclopalladation reaction takes place for a three-coordinate palladium(II) intermediate with the reacting hydrocarbon group entering the vacated fourth coordination site.

Discussion

The reaction of $[PdCl_4]^{2-}$ with 8-methylquinoline (8Me-quin) occurs smoothly in methanol at room temperature to give palladation at the 8-methyl group with liberation of HCl (reaction 1) [1a], and 8-ethylquinoline behaves similarly [1b]:

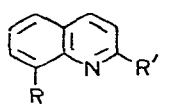


(1)

We have already shown that complexes of 8Me-quin and palladium(II) and

0022—328X/81/0000—0000/$02.50,

other square planar d^8-metal complexes can be isolated in spite of a destabilising close approach of the 8Me groups to the metal atoms above the coordination plane [2—4]. There are now many cases of hydrogen atoms of ligands occupying vacant axial coordination sites of square planar complexes and we hoped in this present work to establish whether or not this geometric arrangement can lead directly to Pd—C bond formation. We present evidence to show that, in the cases we have studied, palladation does not occur with this configuration but rather requires the CH_3-group to be positioned in the coordination plane. In the course of this work we have examined the related chemistry of 8Et-quin, 8Pr^i-quin and 2-substituted analogues attempting to obtain Pd—C bonds with these:



2R′,8R-quin

R = Me; R′ = H, Me, Br, CHO, CHNMe, CH_2OH, CO_2H

R = Et; R′ = H, Me, CHO, CHNMe, CH_2OH, CO_2H

R = Pr^i; R′ = H, Me, CHO, CHNMe

We will present first a description of the metallation reactions and their products followed by a discussion of the mechanism of metallation, drawing together and extending ideas presented elsewhere in communications [5—6].

Results

Palladium behaviour of 8R-quin (R = Me, Et or Pr^i)

8Me-quin reacts smoothly with palladium acetate in methanol, chloroform or dichloromethane at room temperature or above to give the metallated compound $[Pd(OAc)(8Me\text{-}quin\text{-}H)]_2$, complex 1. A solution of these reagents (8Me-quin/Pd 1.00) in $CDCl_3$ showed a decrease in the intensity of the ^1H NMR signals due to the starting materials with an increase in those for 1 with no detectable concentration of any intermediate. Approximately measured kinetics showed first order dependence of rate on both reagents.

Complex 1 exists as a rapidly interconverting mixture of *cis* and *trans* isomers, each of the folded or "basket" type of structure common for acetate-bridge dimers of this sort. A single broad 8-CH_2 ^1H NMR signal is observed at +80°C. At —30°C AB quartets are observed for each isomer separately (Table 1). We assume a greater chemical shift separation within the AB quartet of the *trans*-isomer since one of the hydrogen atoms of each CH_2 group in this isomer lies over an aromatic ring and experiences significant shielding (signal at δ 2.50 ppm compared with δ 3.42, 3.36 and 3.75 ppm for the other three signals). The behaviour giving the NMR coalescences is indicated in Fig. 1. The faster process with a coalescence temperature between —30 and +40°C leads to exchange of H^A and H^B for each isomer separately, the configurations of the Pd atoms being maintained. It is likely that this does not occur by an inversion of the 8-membered rings without bond-breaking, but rather by the mechanism deduced for other acetate-bridged dimers of palladium, that is by opening of one of the acetate bridges, rotation about Pd—O bonds in the remaining bridge and remaking of the double bridge. In view of previous detailed work in this area [8,9] we did not study our system in any more detail. *cis—trans*-Isomerism

TABLE 1

^{1}H NMR DATA OF METALLATED COMPOUNDS [a]

Compound	Chemical shifts (δ, ppm)					
	2-H	4-H	3-H	5,6,7-H	8-R	Other signals
1 [c] *cis*	8.01dd	7.79dd		(6.5—7.4)	3.36d 3.75d	OAc: 2.14s
trans	8.50dd	7.85dd		(6.5—7.4)	2.50d 3.42d	OAc: 2.14s
3	9.58m	8.25dd		(7.2—7.6)	3.12d	^3J(P—CH_2) 3.8 Hz. PEt_3: 1.90m, 1.25m
5	8.02dd	8.26dd		(7.2—7.7)	4.55q 1.27d	
6	9.54m	8.19dd		(7.1—7.7)	3.38quin 1.15t	^3J(P—CH) 7.1 Hz. PEt_3: 1.95m, 1.25m
2 CO_2H, 8 Me-quin	—	8.37d	8.25d	(7.4—7.9)	2.79s	
12	—	8.32d	8.04dd [b]	(7.3—7.7)	3.39d	^3J(P—CH_2) 3.4 Hz. PEt_3: 1.84m, 1.20m
2 CO_2H, 8 Et-quin	—	8.40d	8.25d	(7.4—7.9)	3.30q 1.41t	
14	—	8.31d	8.04d	(7.3—7.8)	3.40quin 1.35t	^3J(P—CH) 7.5 Hz.
2 CH_2OH, 8 Me-quin	—	8.08d	7.20d	(7.4—7.7)	2.78s	2-CH_2OH: 4.85s
9	—	8.04d		(7.2—7.6)	3.15d	^3J(P—CH_2) 3.5 Hz. 2-CH_2OH: 5.05s PEt_3: 1.90m, 1.20m

[a] Recorded at 100 Hz on a Varian HA100 spectrometer in $CDCl_3$ at 27°C. [b] ^5J(P—H) = 0.9 Hz. [c] Ratio of *trans/cis* 4.

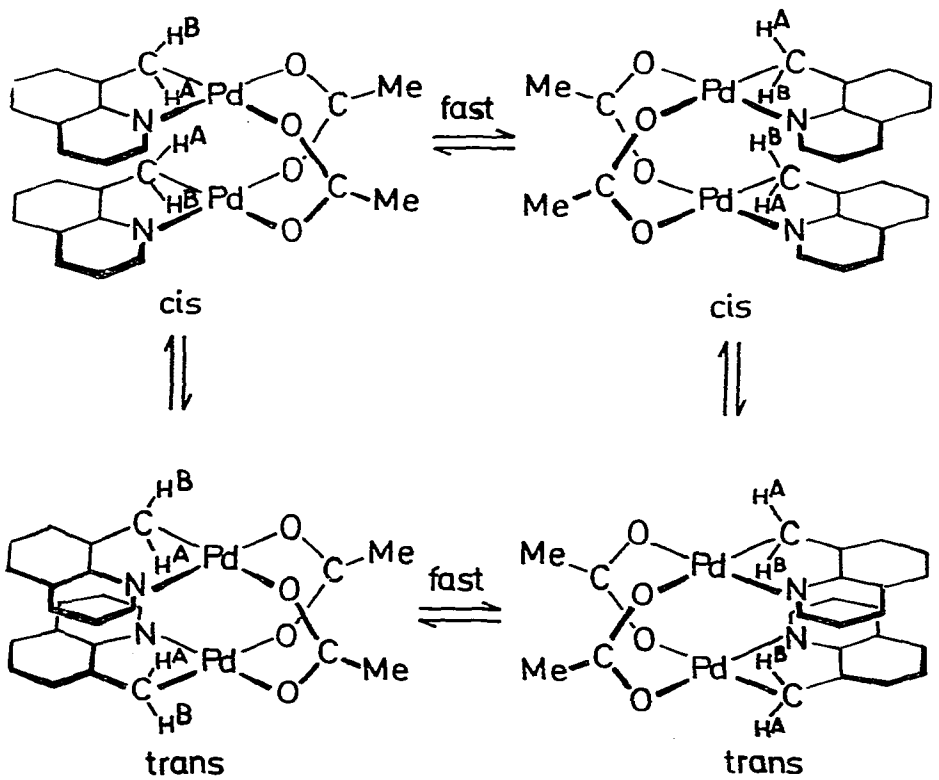


Fig. 1. Dynamic behaviour of complex **1**.

TABLE 2

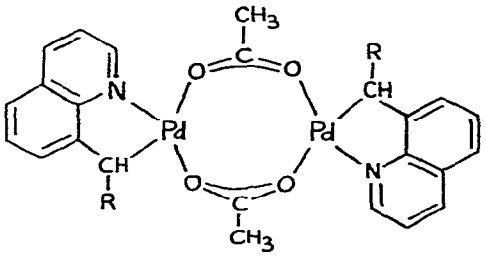
^{13}C NMR DATA (δ, ppm) OF LIGANDS AND METALLATED COMPOUNDS [a]

Compound	2-C	9-C	4-C	8-C	3-C [b]	10-C	5-C	6-C	7-C	8-R [c]	
8 Me-quin	149.1	147.4	136.0	137.1	120.7	128.2	125.8	126.2	129.5	18.1	
8 Et-quin	149.1	147.4	136.0	142.9	120.6	128.3	125.7	126.3	127.9	24.6	
										15.1	
8 Pr^i-quin	149.1	146.2	136.3	147.3	120.6	128.37	125.1	125.5	126.4	27.2	
										23.5	
2 CH_2OH, 8 Me-quin	157.6	145.3	136.8	136.1	117.7	127.3	125.6	125.5	129.8	17.7	2-CH_2OH: 64.8
2 CO_2H, 8 Me-quin	144.9	144.7	139.2	137.2	118.8	130.1	125.9	129.1	131.2	17.7	2-COOH: 164.5
2 CO_2H, 8 Et-quin	144.7	144.3	139.4	143.0	118.8	130.2	125.9	129.3	129.5	24.4	2-COOH: 164.5
										14.8	
3	149.7	148.3	137.7	148.3	121.3d	129.0	123.7	127.6	129.3	24.3d	$P(CH_2CH_3)_3$: 8.3s
					(2.9)					(4.7)	15.8d(29.3)
6	149.8	149.8	137.5	154.7	121.5d	129.2	124.1	127.2	128.0	28.4	$P(CH_2CH_3)_3$: 8.3s
					(3.0)					27.6	15.6d(28.6)
9	149.6	146.8	138.1	147.9	123.1d	128.0	123.5	126.5	127.5	24.7d	$P(CH_2CH_3)_3$: 8.4s
											16.2d(30.3)
											2-CH_2OH: 65.4
12	149.1	149.8	137.3	149.2	121.6d	129.2	123.4	129.6	130.1	20.3d	$P(CH_2CH_3)_3$: 8.32s
					(2.1)					(7.8)	16.2d(27.9)
											2-COO: 172.0d(3.3)
14	150.0	148.9	137.2	155.0	121.7d	129.5	123.9	128.2	130.1	34.9d	$P(CH_2CH_3)_3$: 8.4s
					(2.5)					(4.8)	15.5d(27.1)
										26.4	2-COO: 171.5d(2.9)

[a] Recorded at 23°C on a Varian CFT20 spectrometer. J in Hz. Assignments for signals in parentheses have not been made. [b] ^4J(P—C) in parentheses. [c] ^2J(P—C) in parentheses.

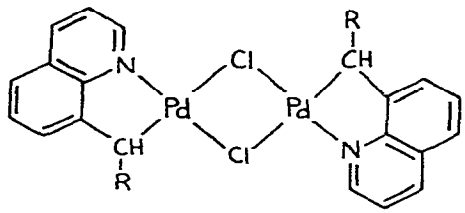
leads to NMR coalescence in the temperature range +40 to +80° C.

Treatment of 1 with LiCl in methanol gave a rapid, almost quantitative, precipitate of $[Pd_2Cl_2(8Me\text{-}quin\text{-}H)_2]$, complex 2, already reported [1] and the chloro bridge of 2 was readily cleaved with PEt_3 (2 mol per mol dimer) to give the soluble complex $[PdCl(8me\text{-}quin\text{-}H)(PEt_3)]$, complex 3. ^1H and ^{13}C NMR spectra of 3 confirmed the formulation (Tables 1 and 2), in particular the 8-CH_2 group gave doublets in both spectra ($^3J(P—CH_2)$ 3.8 and $^2J(P—CH_2)$ 4.7 Hz). The couplings are consistent with the PEt_3 ligand being *cis* to the 8-CH_2 group.



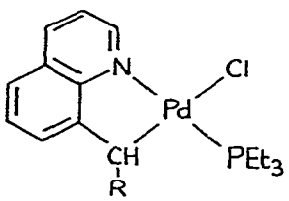
(1) (trans-isomer only shown; R = H)

(4) (R = Me)



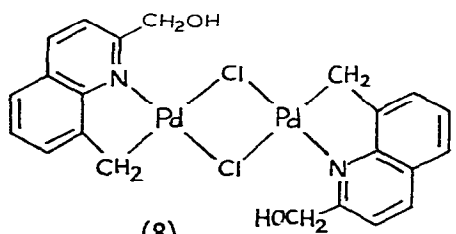
(2) (R = H)

(5) (R = Me)



(3) (R = H)

(6) (R = Me)



(8)

The ligand 8Et-quin reacts with palladium acetate only slightly slower than 8Me-quin to give the metallated complex $[Pd(CH_3CO_2)(8Et\text{-}quin\text{-}H)]_2$, complex 4. This product gives a complex ^1H NMR spectrum even in its low-temperature frozen-out at —30° C which might be expected since three *cis*- and three *trans*-isomers are possible and certainly isomers are present in solution. Treatment of 4 with LiCl gave $[Pd_2Cl_2(8Et\text{-}quin\text{-}H)_2]$, complex 5, which gave a quartet and doublet in the ^1H NMR spectrum as expected for the 8-$CHCH_3$ group. Only one isomer (probably *trans*) is present. Treatment of 5 with PEt_3 gave the very soluble $[PdCl(8Et\text{-}quin\text{-}H)(PEt_3)]$, complex 6, which is structurally analogous to 3. The 8-$CHCH_3$ signal had shifted further on metallation than the 8-CH_2 signal (—13.8 verses —6.3 ppm) which agrees with the generalisation that such shifts are in the order: tertiary > secondary > primary > CH_3 [10].

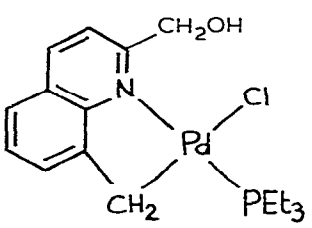
8Pr^i-quin was treated in various ways with palladium(II) compounds unsuccessfully attempting to form Pd—C bonds. Solutions of palladium acetate and 8Pr^i-quin in $CDCl_3$ show no reaction after 3 days at room temperature (^1H

NMR) or after 5 h under reflux except for some Pd metal formation in the latter case. Even after a solution of these reagents in glacial acetic acid was heated at 100°C for 1 h, only 8Pr^i-quin, Pd metal and palladium acetate (60%) were recovered. A solution of 8Pr^i-quin and Na_2PdCl_4 in refluxing methanol (10 h) gave a yellow insoluble precipitate (83%) which was identified as *trans*-$[PdCl_2(8Pr^i\text{-quin})_2]$, complex 7, but no metallation was observed.

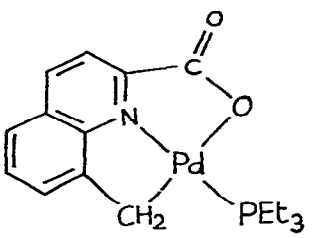
Palladation behaviour of 2-substituted derivatives of 8R-quin (R = Me, Et or Pr^i)

We prepared a range of 2-substituted 8-alkylquinolines to establish whether or not coordinating properties of the 2-substituent R′ are necessary for metallation at the 8R group. For the ligands 2Me,8R-quin (R = Me, Et or Pr^i), 2Br,8Me-quin and 2CHO,8R-quin (R = Me, Et or Pr^i) no metallation was observed with palladium acetate or $Na_2[PdCl_4]$. For example, solutions of 2Me,8Me-quin with palladium acetate in methanol or $CHCl_3$ at room temperature or under reflux (4 h) or in acetic acid at 100°C (1 h) gave only the unreacted quinoline, palladium acetate and some Pd metal. A solution of 2Me,8Me-quin and $Na_2[PdCl_4]$ in refluxing methanol (15 h) gave some decomposition to Pd metal but no metallated complexes. Nor was $[PdCl_2(2Me,8Me\text{-quin})_2]$ precipitated. Similar observations were made on 2CHO,8Me-quin and 2Br,8Me-quin. Almost certainly metallation products would be stable under all these conditions and would have been isolated if formed.

In contrast the ligands $2CH_2OH$,8Me-quin, $2CO_2H$,8R-quin (R = Me or Et) and 2CH=NMe,8R-quin (R = Me, Et or Pr^i) are all palladated with palladium acetate in $CHCl_3$ at room temperature. A $CDCl_3$ solution of $2CH_2OH$,8Me-quin and palladium acetate (equimolar) lightened in colour over 3 h at 25°C while the ^{1}H NMR signals of the free ligand were steadily replaced by those of the product. No intermediate was observed. Work-up gave a sparingly soluble yellow solid of variable analysis which when treated with LiCl in methanol gave $[Pd_2Cl_2(2CH_2OH,8Me\text{-quin-H})_2]$, complex 8. Compound 8 showed ν(OH) at 3410 cm^{-1} in the infrared spectrum indicating the lack of a coordinated CH_2O^- group. $[PdCl(2CH_2OH,8Me\text{-quin-H})(PEt_3)]$, complex 9, was prepared as soluble yellow crystals from 8 by reaction with PEt_3. This was fully characterised by its ^{1}H and ^{13}C NMR spectra; coordinated 8-CH_2 and non-coordinated 2-CH_2OH were identified.



(9)



(12)

A mixture of $2CO_2H$,8Me-quin (2 mol per mol Pd atoms) and palladium

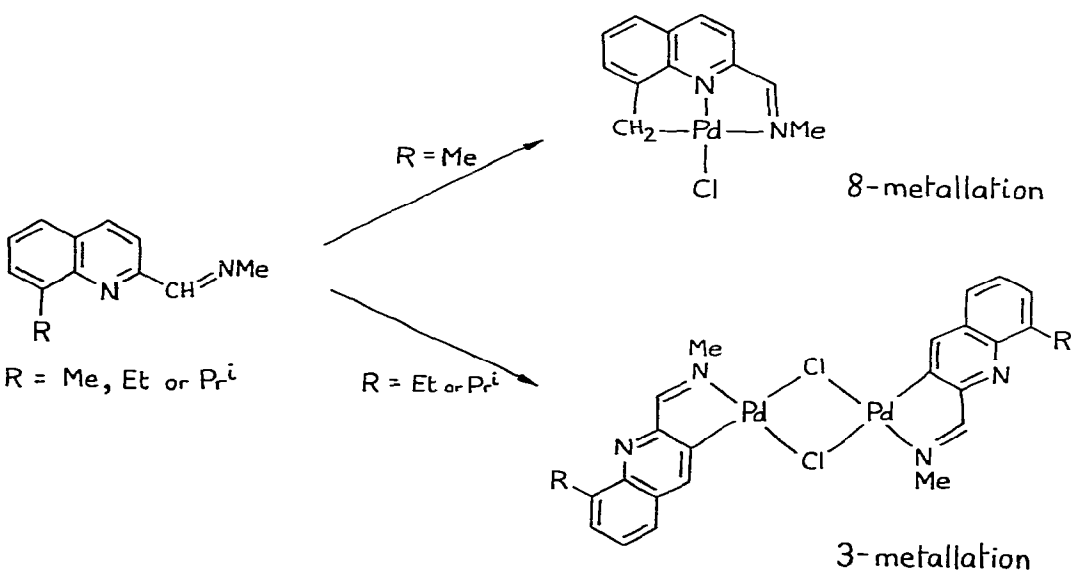
acetate in $CDCl_3$ gave $[Pd(2CO_2,8Me\text{-}quin)_2]_n$, complex **10**, by an exchange reaction (eq. 2).

$$[Pd(CH_3CO_2)_2] + 2(2CO_2H,8Me\text{-}quin) = [Pd(2CO_2,8Me\text{-}quin)_2] + 2CH_3CO_2H \quad (2)$$

(10)

The molecularities of the carboxylato complexes are unknown. Complex **10** could not be isolated because it readily converted into the palladated complex **11**, $[Pd(2CO_2,8Me\text{-}quin\text{-}H^8)]_n$. Mixing $2CO_2$,8Me-quin (1 mol per mol Pd atoms) with palladium acetate rapidly gave a 1/1 mixture of **10** and palladium acetate but on standing for 90 min at 25°C essentially quantitative precipitation of **11** occurred. Complex **11** gave variable analytical results (variable H_2O content) but with PEt_3 gave $[Pd(2CO_2,8Me\text{-}quin\text{-}H^8)(PEt_3)]$ (**12**) which was thoroughly characterised. In particular ^1H and ^{13}C NMR spectra were totally cosistent with the structure shown; ^{31}P coupling to the 2-CO_2 nucleus confirmed tridentate coordination. Analogous complexes $[Pd(2CO_2,8Et\text{-}quin\text{-}H^8)]_m$ (**13**) and $[Pd(2CO_2,8Et\text{-}quin\text{-}H^8)(PEt_3)]$ (**14**) were obtained similarly from $2CO_2$,8Et-quin.

We have previously described the metallation products from 2CH=NMe,8R-quin (R = Me, Et or Pr^i) and their spectroscopic characterisation [11]. Notably with palladium acetate 2CH=NMe,8Me-quin gives 8-CH_3 metallation while metallation occurs at the 3-position when R = Et or Pr^i (Scheme 1). Palladation at the 3-position when R = Me is possible if chloride ions are added to the reaction solution. Table 3 gives the conditions of several experiments on this system leading to various proportions of the 8- and 3-metallated products, each of



Scheme 1. Products from reaction with palladium acetate in $CDCl_3$ and then with lithium chloride in methanol.

which may be obtained exclusively if the conditions are carefully chosen. In general the proportion of 3-metallation increases with increasing amount of chloride present, but so does the amount of non-metallated products. Bromide ions prevent metallation and allowed the isolation of $[PdBr_2(2CH{=}NMe,8Me\text{-}quin)_2]$.

Interestingly a mixture of $[AsPh_4]_2[Pd_2Cl_6]$ and 2CH=NMe,8Me-quin (1 mol per mol Pd atoms) in CH_2Cl_2 was added to a TLC plate (SiO_2) and eluted repeatedly with CH_2Cl_2 to given an orange band of $[PdCl(2CH{=}NMe,8Me\text{-}quin\text{-}H^8)]$ in 46% yield, the remaining organic compound being isolated as the aldehyde. However, $[PdCl_2(2CH{=}NMe,8Me\text{-}quin)]$ did not metallate in refluxing $CHCl_3$ (22 h); 83% was recovered.

Discussion

The mechanism of cyclopalladation will be discussed in the context of these results. Reported evidence is consistent with an electrophilic palladium centre in these reactions [12—13]. Palladium(II) complexes are generally unreactive towards oxidative addition so that cyclopalladations are best envisaged as electrophilic substitutions with transition states such as those in Fig. 2. The stereochemical change at carbon is unknown. It is likely that the displaced H^+ combines with *cis*-coordinated or external anion X in mechanisms (A) and (B) respectively.

(a) Nature of the metallated group. Metallation rates decrease in the order Me ≳ Et >> Pr^i for 8-alkyl-quinolines and similarly for 2CH=NMe,8R-quin metallation at R only occurs for R = Me (Scheme 1). This could reflect the relative abilities of these ligands to coordinate prior to metallation. We have shown for reaction 3 that the equilibrium constants are in the order L = 8Me-quin > 8Et-quin > 8Pr^i-quin, but the differences are not large [14]. K[8Me-quin]/K[8Et-quin] = 20 whereas K[8Et-quin]/K[8Pr^i-quin] = 6. Thus Pr^i-quin is not

$$Rh_2Cl_2(CO)_4 + 2L \rightleftharpoons 2RhCl(CO)_2L \qquad (3)$$

much poorer as a ligand than 8Et-quin and indeed we have isolated *trans*-$[PdCl_2(8Pr^i\text{-}quin)_2]$. There must be reasons other than poor coordination why Pr^i-quin is not metallated. Coordination 8Pr^i-quin must be predominantly in

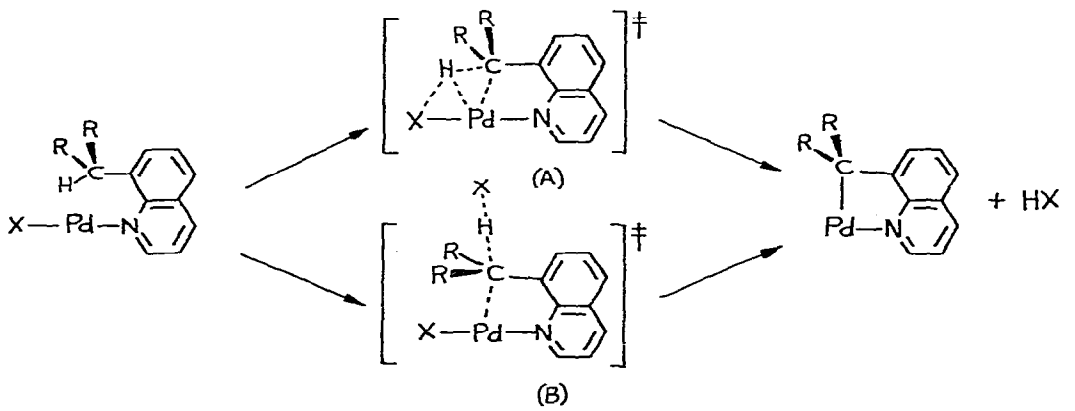
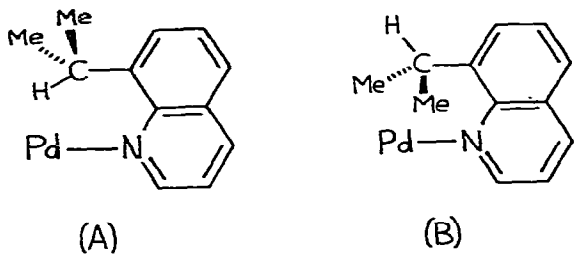


Fig. 2. Possible transition states for electrophilic palladation.



(A) (B)

Fig. 3. Conformations of coordinated 8Pr^i-quin.

conformation (A) rather than (B) or any other conformation with Me groups close to Pd (Fig. 3). Conformation (A) was found for [Pd(η^3-allyl)(2CH=NMe, 8Pr^i-quin)][ClO_4] in the crystal [11]. This conformation is ideally set-up for attaining the transiton state (A) and from this it might seem that cyclopalladation requires a transition state (A) and from this it might seem that cyclopalladasteric effects on changing from Et to Pr^i cannot be separated and so we cannot rule out electronic reasons for the lack of metallation of Pr^i-quin.

(b) Metal···H—C interactions prior to cyclometallation. We have sought evidence concerning such interactions in d^8-complexes. The close approach of the H—C group to metal atoms in an axial direction is destablishing for square-planar palladium(II) and our attempts to enforce such interactions in the coordination plane by use of chelating ligands have lead to interesting results but not to hydrogen bridges. Bidentate coordination of 2CH=NMe,8Pr^i-quin [11], 2$CH_2PBu^t_2$,8Me-quin [15], and di-2,2'-(8Me-quinolyl) [16] at palladium is achieved by having marked distortions in the metal to nitrogen coordination which lead to increase in the distance of the 8R-group from the metal atom. These systems are well set-up for hydrogen bridges as in Fig. 4 but in view of there being considerable distortions to avoid such interactions and to retain normal four-coordination we feel that such CH—Pd interactions are destabilising or only weakly stabilising. The only possible case of hydrogen bridges to the metal that we have observed is in [$Rh_2Cl_2(CO)_3$(2$CH_2PBu^t_2$,8Me-quin)] in which there is coupling of the 8Me group to ^{103}Rh and ^{31}P in the ^{9}H and ^{13}C NMR spectra [15]. In spite of these results, we believe that the formation of three-coordinate palladium is necessary for cyclopalladation and that this could be somewhat assisted by forming hydrogen bridges. There is now a lot of evidence for stabilising interactions of this sort with other unsaturated metal atoms.

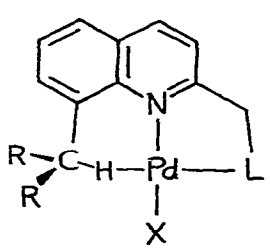


Fig. 4. Possible ground state interactions in chelating 8-alkylquinoline based ligands.

(c) Nature of the metal complex in the cyclometallation step. Addition of 2CH=NMe,8Me-quin (2 mol per mol Pd atoms) to palladium acetate gives *trans*-$[Pd(OAc)_2(2CH{=}NMe,8Me\text{-}quin)_2]$ which undergoes cyclopalladation more slowly than when there is one ligand molecule per Pd atom. Usually $[PdCl_2L_2]$ complexes cyclometallate less readily than when L/Pd = 1. This might indicate the need for a vacant in-plane coordination site for cyclometallation and we wish to argue that a three-coordinate intermediate is required. Cope has showed that two amine ligands per Pd atom are required [17,18], but this applies to basic ligands for which the extra molecule of ligand is required to neutralise the HCl formed. If NEt_3 is added, only one mol equivalent of ligand is required.

We have observed that the nature of the 2-substituent in 2R,8Me-quin is of prime importance in controlling whether or not there is 8-metallation. When the 2-substituent is Me, Br or CHO, metallation is totally prevented. Although the 2Me-group increases the basicity of the quinoline, it impairs its coordinating ability for steric reasons [14], but not sufficiently to prevent coordination. The reason the 2Me-group prevents metallation is as follows. We propose that a ligand *cis* to 8Me-quin coordinated in its usual vertical conformation is lost so as to allow the quinoline to rotate into the coordination plane, the 8Me-group then occupying the vacated *cis*-position. It is in this configuration that electrophilic substitution proceeds. With 2Me,8Me-quin the 2Me-group clashes with the remaining *cis*-ligand and makes rotation into the in-plane conformation more difficult than for 8Me-quin. The 8Me-quin and 2Me,8Me-quin complexes of type shown in Fig. 5 have been prepared [3]. For 8Me-quin (R = H) the process shown occurs rapidly giving ^1H NMR coalescence of the two NMe_2 singlets but for 2Me,8Me-quin (R = Me) the process is too slow even at elevated temperatures to give any NMR line-broadening. This process requires the loss of the *cis*-H_2O ligand and quinoline rotation about the Pd—N bond so that this ligand passes into and through the coordination plane. This dynamic process and cyclometallation both require the same in-plane ligand conformation and the marked reduction in rate on introducing the 2Me-group is the same for both.

In contrast to the above behaviour, where the 2-substituent of 2R,8Me-quin is CH=NMe, CO_2H or CH_2OH cyclopalladations do occur and at similar rates to 8Me-quin. It is curious that in the systems described in this paper cyclopalladations either occur at very similar rates or not at all. The need for bidentate

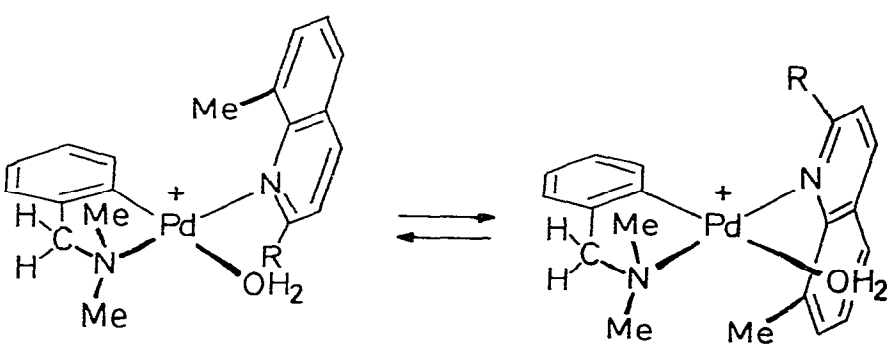


Fig. 5. Dynamic behaviour of certain 8-methylquinoline complexes.

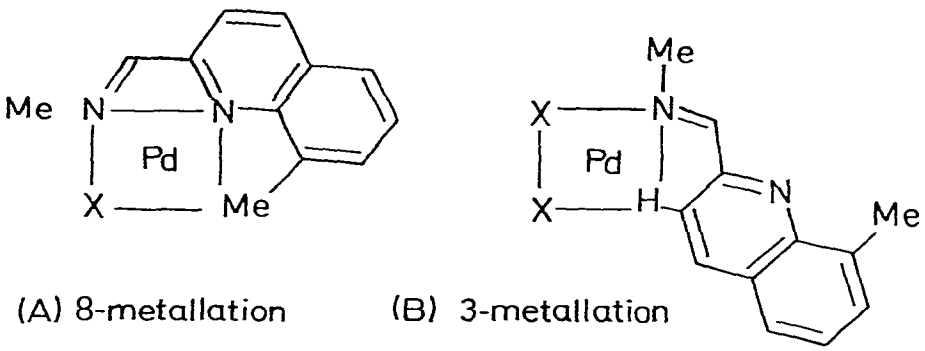


Fig. 6. Probable arrangements leading to 8- and 3-metallation of 2CH=NMe,8Me-quin.

coordination of these ligands for 8-metallation is further suggested by the increasing proportion of 3-metallation of 2CH=NMe,8Me-quin on increasing the Cl/Pd ratio (Table 3). Thus one more coordination site seems to be required for 8-metallation via (A) (Fig. 6) than for 3-metallation by (B), although a different dependence upon [Cl^-] in the rate of loss of HCl from aromatic than from alkyl groups cannot be discounted as a source of these differences. The observation that [$PdCl_2$(2CH=NMe,8Me-quin)] does not cyclopalladate at all in refluxing chloroform while a similar reflux in methanol gives 8-metallation (37%) and 3-metallation (16%) implies a polar solvent is needed, possibly to generate in-plane sites by solvolysis of chloride ligands.

The cyclopalladation reaction of benzo[*h*]quinoline is another interesting case because coordination through palladium would seem to require that the metal atom approach the hydrogen rather than the carbon atom of the C—H

TABLE 3

THE PALLADATION OF 2 CH=NMe,8Me-quin (L) UNDER VARIOUS CONDITIONS

Amounts of reagents (mmol)				Solvent and conditions	Products (%)		
L	Pd	X^-	X/Pd		3-met	8-met	[PdX_2L_2] or [PdX_2L]
2.7	2.7	10.8(Cl)	4.0	Methanol (60 cm^3) 20 h reflux	23	17	0
2.7	2.8	15.1(Cl)	5.5	Methanol (30 cm^3) 15 h reflux	52	0	16 [a]
2.7	2.8	5.6(Cl) 9.1(Br)	2.0(Cl) 3.6(Br)	Methanol (20 cm^3) 25 h reflux	0	0	68 [b]
0.21	0.21	0.63(Cl)	3.0	TLC using CH_2Cl_2	0	46	0
1.09	1.04	2.08(Cl)	2.0	$CHCl_3$ (25 cm^3) 22 h reflux	0	0	83 [c]
0.83	0.83	1.66(Cl)	2.0	Methanol (25 cm^3) 22 h reflux	16	37	0
4.5	4.5	9.0(OAc)	2.0(OAc)	$CHCl_3$ (50 cm^3) 1 h, 40°C	0	95	0

[a] [$PdCl_2L_2$]. [b] [$PdBr_2L_2$]. [c] [$PdCl_2L$].

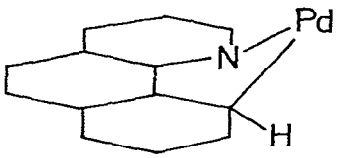


Fig. 7. Geometry during the palladation of benzo[*h*]quinoline.

bond to be cleaved. However, the easy geometric distortion at nitrogen that we have observed for palladium-coordinated bis-2,2'-(8-methylquinolyl) [16] and in other cases [11,15] suggests that the geometry such as shown in Fig. 7 is accessible during the palladation reaction.

Conclusions

Cyclopalladations of 8-alkylquinolines are electrophilic in character and for unknown reasons the Pr^i group of 8Pr^i-quin is deactivated to CH cleavage. Of the two possible intimate mechanisms (both S_E2) leading to displacement of H^+ by Pd^{II}, one with and the other without inversion at carbon, no distinction could be made, except that it is geometrically impossible for 8Pr^i-quin to undergo inversion. This could imply the inversion pathway is occurring in cyclopalladations, but in the absence of studies on optically active centres the problem remains open. The metallation step only occurs when the alkyl group can enter the coordination plane of the Pd atom, so that the metallating agent is a highly unsaturated 14*e*-metal system.

Experimental

Ligand syntheses

8Me-quin (Koch-Light) was obtained commercially, but 8Et-quin, 8Pr^i-quin, 2Me,8R-quin (R = Me, Et or Pr^i), 2CHO,8R-quin (R = Me, Et, or Pr^i) and their methylimines were prepared by methods we have already described [11]. 2CO_2H,8R-quin (R = Me or Et) were prepared (>90% yield) from the corresponding aldehydes by oxidation with an excess of aqueous H_2O_2 in acetone followed by recrystallisation from petroleum ether to give white crystals; R = Me (Found: C, 69.6; H, 4.9; N, 7.0. $C_{11}H_9NO_2$ calcd.: C, 70.6; H, 4.85; N, 7.5%) R = Et (Found: C, 70.55; H, 5.8; N, 6.65. $C_{12}H_{11}NO_2$ calcd.: C, 71.6; H, 5.5; N, 6.95%).

2CH_2OH,8R-quin (R = Me or Et) were also prepared (>90% yield) from the aldehydes by reduction with $NaBH_4$ in 1-methylethanol. Addition of water and extraction with chloroform gave the alcohols as white crystals; R = Me (Found: C, 75.85; H, 6.4; N, 7.95. $C_{11}H_{11}NO$ calcd.: C, 76.25; H, 6.4; N, 8.1%), R = Et (Found: C, 76.6; H, 7.15; N, 7.35. $C_{12}H_{13}NO$ calcd.: C, 77.0; H, 7.0; N, 7.5%).

Metallation and attempted metallation reactions

8Me-quin. The reaction of $[PdCl_4]^{2-}$ has been described [1]. A solution of palladium acetate (0.5 g) and 8Me-quin (0.33 g) in methanol (25 cm^3) was

warmed at 50°C for 1 h by which time the dark solution had become orange. Removal of solvent under vacuum and addition of diethyl ether to the residue gave a yellow solid which gave deep yellow crystals of [Pd(8Me-quin-H)-(OAc)]$_2$, complex 1, (0.62 g, 88%) from chloroform/ether mixtures (Found: C, 46.75; H, 3.75; N, 4.65. $C_{24}H_{22}N_2O_4Pd_2$ calcd.: C, 46.85; H, 3.6; N, 4.55%).

Addition of LiCl (excess) in methanol to complex 1 in methanol gave an immediate and almost quantitative precipitation of [Pd(8Me-quin-H)Cl]$_2$, complex (2), as a pale yellow powder (Found: C, 42.35; H, 2.95; N, 4.85; Cl, 12.55. $C_{20}H_{16}Cl_2N_2Pd_2$ calcd.: C, 42.3; H, 2.85; N, 4.95; Cl, 12.5%).

Addition of PEt_3 (1 mol per mol Pd atoms) to a chloroform suspension of 2 gave [Pd(8Me-quin-H)Cl(PEt_3)], compound 3, as well formed colourless crystals from chloroform/ether mixtures (Found: C, 47.85; H, 6.0; N, 3.35; Cl, 8.7; P, 7.9. $C_{16}H_{23}ClNPPd$ calcd.: C, 47.8; H, 5.75; N, 3.5; Cl, 8.8; P, 7.7%).

8Et-quin. A solution of 8Et-quin (0.37 g) and palladium acetate (0.50 g) in chloroform (30 cm^3) was warmed at 30 to 40°C for 1 h to give an orange solution from which the solvent was removed under vacuum. Addition of diethyl ether gave an orange solid which was recrystallised from chloroform/ether mixtures to give [Pd(8Et-quin-H)(OAc)]$_2$, compound 4, as yellow microcrystals (0.70 g, 95%).

As for the 8Me-quin compounds, compounds 5 and 6, were prepared by successive additions of LiCl (excess) and PEt_3 (1 mol per mol Pd atoms). (Found for 5: C, 43.65; H, 3.35; N, 4.65; Cl, 12.25. $C_{22}H_{20}Cl_2N_2Pd_2$ calcd.: C, 44.35; H, 3.35; N, 4.7; Cl, 11.9%. Found for 6: C, 48.9; H, 6.2; N, 3.25; Cl, 8.4; P, 7.65. $C_{17}H_{25}ClNPPd$ calcd.: C, 49.05; H, 6.05; N, 3.35; Cl, 8.5; P, 7.45%).

8Pr^i-quin. The ^{1}H NMR spectrum of a solution of palladium acetate (0.50 g) and 8Pr^i-quin (0.40 g) in $CDCl_3$ (30 cm^3) kept at 30°C was recorded periodically over 3 days and then after 5 h under reflux. No reaction occurred except for some decomposition to Pd metal. Further, a solution of palladium acetate (0.20 g) and 8Pr^i-quin (0.16 g) in neat glacial acetic acid (10 cm^3) was heated at 100°C for 1 h. Workup gave only 8Pr^i-quin, palladium acetate (50% recovery) and Pd metal.

A solution of $Na_2[PdCl_4]$ (0.59 g) and 8Pr^i-quin (0.50 g) in methanol (50 cm^3) was heated under reflux for 10 h to give a precipitate of *trans*-[$PdCl_2$(8Pr^i-quin)$_2$], compound 7, (0.50 g, 83% based on ligand) (Found: C, 54.6; H, 5.1; N, 5.65; Cl, 14.0. $C_{24}H_{26}Cl_2N_2Pd$ calcd.: C, 55.45; H, 5.05; N, 5.4; Cl, 13.65%).

Metallation reactions of 2CH=NMe,8Me-quin

This reaction was extensively studied; see Table 3 and ref. 11.

1. With palladium acetate. A solution of palladium acetate (1.0 g) and ligand (0.9 g) in chloroform (50 cm^3) was heated at 40°C for 1 h. The solvent was removed from the cooled and filtered solution and the residue gave deep red crystals (1.56 g, 95%) of [Pd(2CH=NMe,8Me-quin-H^8)(OAc)(H_2O)] from benzene/diethyl ether. Similar reactions with the 8Et and 8Pr^i analogues gave 3-metallated products.

2. With $Na_2[PdCl_4]$. A solution of $Na_2[PdCl_4]$ (0.75 g) and ligand (0.5 g) in methanol (60 cm^3) was refluxed for 20 h to give a yellow precipitate (0.38 g). Soxhlet extraction of this solid with CH_2Cl_2 gave the more soluble

[PdCl(2CH=NMe,8Me-quin-H^8)] (0.15 g) as an orange solid and [PdCl(2CH=NMe,8Me-quin-H^3)]$_2$ (0.20 g) as a yellow solid. The deep red methanolic mother liquor gave after chromatography the dimethylacetal of 8-methylquinoline-2-carboxaldehyde as a colourless oil (0.16 g) (Found: C, 71.7; H, 6.95; N, 6.4. $C_{13}H_{15}NO_2$ calcd.: C, 71.85; H, 6.95; N, 6.45%), and a red solid (0.37 g) presumed to contain $[PdCl_4]^{2-}$.

3. On silica. A solution of ligand (0.04 g) and $[AsPh_4]_2[Pd_2Cl_6]$ (0.126 g) in CH_2Cl_2 (0.5 cm^3) was added to a silica TLC plate and eluted repeatedly with CH_2Cl_2. From the two main bands were obtained 2CHO,8Me-quin (0.02 g, 50%) and [PdCl(2CH=NMe-quin-H^8)] (0.032 g, 46%) as an orange powder.

4. With an excess of LiCl. A solution of $PdCl_2$ (0.5 g), LiCl (0.4 g) and ligand (0.5 g) in methanol (30 cm^3) was refluxed for 15 h. The yellow precipitate (0.60 g) was treated with pyridine to give [PdCl(2CH=NMe,8Me-quin-H^3)(Py)] (0.57 g, 52%) leaving behind insoluble [$PdCl_2$(2CH=NMe,8Me-quin)$_2$] (0.12 g, 16%).

5. With LiBr. A solution of $PdCl_2$ (0.5 g), LiBr (0.8 g) and ligand (0.5 g) in methanol (30 cm^3) was refluxed for 25 h. The white solid below the red solution was filtered off, washed with methanol and diethylether, and shown to be [$PdBr_2$(2CH=NMe,8Me-quin)$_2$] (0.55 g, 68%).

6. With [$PdCl_2$(PhCN)$_2$]. A solution of the bis-benzonitrile compound (0.40 g) and ligand (0.2 g) in chloroform (25 cm^3) was refluxed for 22 h. [$PdCl_2$(2CH=NMe,8Me-quin)] was obtained as an orange precipitate (0.30 g, 83%). A solution of this complex (0.30 g) in methanol (25 cm^3) was refluxed for 22 h to give insoluble solids (0.18 g), which were separated into [PdCl(2CH=NMe,8Me-quin-H^3)(py)] (0.10 g, 37%) and [PdCl(2CH=NMe,8Me-quin-H^8)] (0.075 g, 16%) by treatment with pyridine.

Metallation of 2CO_2H,8Me-quin

A solution of palladium acetate (0.22 g) and ligand (0.19 g, 1 mol per mol Pd atoms) in $CHCl_3$ (15 cm^3) after 3 h at 30°C gave a pale yellow precipitate of [Pd(2CO_2,8Me-quin-H^8)]$_m$ (11) (0.23 g, 81%) (Found: C, 43.95; H, 2.55, N, 4.8. $C_{11}H_7NO_2Pd$ calcd.: C, 45.3; H, 2.4; N, 4.8%). Treatment with PEt_3 (1 mol per mol Pd) gave [Pd(2CO_2,8Me-quin-H^8)(PEt_3)] (12) as white crystals from chloroform-ether mixtures (Found: C, 49.7; H, 5.3; N, 3.3; P, 7.7. $C_{17}H_{22}NO_2P$-Pd calcd.: C, 49.7; H, 5.4; N, 3.4; P, 7.6%).

Similar reactions using 2CO_2H,$_8$Et-quin gave [Pd(2CO_2,8Et-quin-H^8)]$_m$ (13) (0.21 g, 72%) (Found: C, 46.0; H, 2.95; N, 4.3. $C_{12}H_9NO_2Pd$ calcd.: C, 47.15; H, 2.95; N, 4.6%) and [Pd(2CO_2,8Et-quin-H^8)(PEt_3)] (14) (Found: C, 51.0; H, 5.7, N, 3.3; P, 7.3. $C_{18}H_{24}NO_2PPd$ calcd.: C, 50.9; H, 5.55; N, 3.65; P, 7.6%).

Metallation of 2CH_2OH,8Me-quin

A solution of ligand (0.50 g) and palladium acetate (0.70 g) in chloroform (20 cm^3) lightened in colour on standing for 3 h at 30°C. Removal of solvent under vacuum gave a yellow solution which could not be redissolved but treatment of a suspension in methanol with an excess of LiCl gave [PdCl(2CH_2OH, 8Me-quin-H^8)]$_2$ (8) as a new precipitate (Found: C, 41.6; H, 3.3; N, 4.25; Cl, 11.05. $C_{22}H_{20}Cl_2N_2O_2Pd_2$ calcd.: C, 42.05; H, 3.2; N, 4.45; Cl, 11.3%). Treatment of 8 with PEt_3 (1 mol per mol Pd) gave [Pd(2CH_2OH,8Me-quin-H^8)-

(PEt_3)] (9) as yellow crystals from chloroform/ether mixtures (Found: C, 47.0; H, 5.85; N, 3.05; Cl, 8.45; P, 7.55. $C_{17}H_{25}ClNOPPd$ calcd.: C, 47.25; H, 5.85; N, 3.25; Cl, 8.2; P, 7.2%).

Acknowledgements

We thank Johnson-Matthey Ltd for a generous loan of $PdCl_2$ and the S.R.C. for a studentship (I.P.R.).

References

1 (a) G.E. Hartwell, R.V. Lawrence and M.J. Smas, Chem. Commun., (1970) 912; (b) V.I. Sokolov, T.A. Sorokina, L.L. Troitskaya, L.I. Solovieva and O.A. Reutov, J. Organometal. Chem., 36 (1972) 389.
2 A.J. Deeming, L.P. Rothwell, M.B. Hursthouse and L. New, J. Chem. Soc. Dalton, (1978) 1490.
3 A.J. Deeming and I.P. Rothwell, J. Chem. Soc. Dalton, (1978) 1497.
4 A.J. Deeming and I.P. Rothwell, Inorg. Chim. Acta, 31 (1978) 271.
5 A.J. Deeming and I.P. Rothwell, J. Chem. Soc. Chem. Commun., (1978) 344.
6 A.J. Deeming and I.P. Rothwell, Pure Appl. Chem., 52 (1980) 649.
7 M.R. Churchill and R. Mason, Nature, 204 (1964) 777.
8 J. Powell and T. Jack, Inorg. Chem., 11 (1972) 1039.
9 J. Powell, J. Amer. Chem. Soc., 91 (1969) 4311.
10 M.H. Chisholm and S. Godslenski, Prog. Inorg. Chem., 20 (1976) 299.
11 A.J. Deeming, I.P. Rothwell, M.B. Hursthouse and K.M.A. Malik, J. Chem. Soc. Dalton, (1979) 1899.
12 M.I. Bruce, B.L. Goodall and F.G.A. Stone, J. Chem. Soc. Chem. Commun., (1973) 558; J. Chem. Soc. Dalton, (1978) 687.
13 S. Hietkamp, D.J. Stufkens and K. Vrieze, J. Organometal. Chem., 168 (1979) 351.
14 A.J. Deeming and I.P. Rothwell, J. Chem. Soc. Dalton, (1980) 1259.
15 A.J. Deeming, I.P. Rothwell, M.B. Hursthouse and K.M.A. Malik, J. Chem. Soc. Dalton, in press.
16 A.J. Deeming, I.P. Rothwell, M.B. Hursthouse and J.D.J. Backer-Dirks, J. Chem. Soc. Chem. Commun., (1979) 670.
17 A.C. Cope and M. Dubeck, J. Amer. Chem. Soc., 87 (1965) 3272.
18 A.C. Cope and E.C. Friedrich, J. Amer. Chem. Soc., 90 (1968) 909.