Co-ordination Chemistry of (8-Methyl-2-quinolylmethyl)di-t-butylphosphine (mqp) with Palladium, Rhodium, Iridium, and Manganese: Crystal Structure of $[PdCl_2(mqp)]$ †

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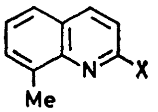
Complexes of the new title ligand (mqp) have been synthesised which contain unidentate, bidentate, or 3-metallated modes of co-ordination as established by ^1H and ^{13}C n.m.r. data. The complex $[PdCl_2(mqp)_2]$ contains unidentate mqp while $[PdCl_2(mqp)]$ (as a CH_2Cl_2 solvate) contains bidentate mqp as shown by a single-crystal structure determination. Crystals are monoclinic, space group $P2_1/c$, with a = 12.936(3), b = 13.108(3), c = 15.085(3) Å, β = 100.48(2)°, and Z = 4. The structure has been determined by Patterson and Fourier methods and refined by least squares to R 0.047 for 3 490 diffractometer data. In-plane bidentate co-ordination would require a considerable clash of mqp with one *cis* Cl, but distortions within the still essentially square-planar complex reduce this clash. A small pyramidal distortion at the co-ordinated nitrogen atom contributes to this reduction. This complex yields 3-metallated $[Pd_2Cl_2(mqp\text{-}H^3)_2]$ in refluxing alcohols in the presence of lithium acetate, but in the absence of the latter the HCl formed leads to the quinolinium salt of the 3-metallated product. Various chlorocarbonyl derivatives of $[Rh_2Cl_2(CO)_4]$ are described, the most significant being $[Rh_2Cl_2(CO)_3(mqp)]$ which contains bidentate mqp and shows nuclear spin–spin coupling between the nuclei of the 8-Me group and the ^{103}Rh and ^{31}P nuclei, indicating a significant interaction between the non-metallated Me group and the metal atom. 3-Metallated mqp complexes of iridium(III) and of manganese(I) are also described.

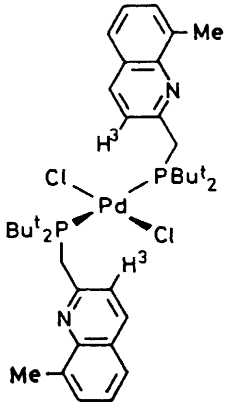
In a survey of the co-ordination behaviour of 8-alkylquinolines we have synthesised 2-substituted derivatives of 8-methylquinoline that are potentially bidentate. We have already described[1] chemistry of the 2-X-substituted quinolines where X is the imine group CH=NMe and now report related chemistry for the title ligand mqp which has X = $CH_2PBu^t_2$. Apart from the advantage of relatively simple ^1H and ^{13}C n.m.r. spectra, we expected that the bulky Bu^t groups would favour bidentate co-ordination (ring formation) and so we would be able to study interactions between the 8-methyl group and the metal atom in complexes with co-ordinated quinoline. The methyl group would be positioned *trans* to the phosphine and, since large nuclear spin–spin coupling constants between mutually *trans* ligands are normal, any covalency between the methyl group and the metal atoms might be detected by ^{31}P coupling to the ^{13}C and ^1H nuclei of the 8-substituent.



X = CH=NMe (mqa)
X = $CH_2PBu^t_2$ (mqp)

RESULTS AND DISCUSSION

Palladium(II) *Complexes of mqp*.—The addition of 2 equivalents of mqp to a methanolic solution of $Na_2[PdCl_4]$ gave a pale yellow precipitate of *trans*-$[PdCl_2(mqp)_2]$ (1), containing mutually *trans* unidentate ligands as shown by triplets due to virtual ^{31}P coupling for the signals PCH_2, $PC(CH_3)_3$, and $PC(CH_3)_3$ in the ^1H and ^{13}C n.m.r. spectra (Tables 1 and 2) and a single ν(Pd–Cl) absorption at 345.5 cm⁻¹ (Table 3). The absence of Pd–N bonding is inferred from the negligible shifts for the 8-Me group on complex formation and the presence of a downfield shift for the 3-H signal compared with that of the free ligand. This downfield shift is much smaller than that observed for unidentate mqa[1] and we believe that this is due to the rotational flexibility about the $P\text{–}CH_2\text{–}C$ bonds which allows the average position of the 3-H to be further from the metal atom. Low-temperature ^1H n.m.r. spectra failed to reveal separate rotamers as with other PBu^t_2X square-planar complexes.[2,3] The co-ordination of the phosphorus atom of mqp in (1) leads to characteristic changes in n.m.r. spectra as in other Bu^t and benzyl phosphines.[4,5] The PCH_2 shifts downfield and its ^{31}P coupling is increased from 3.5 to 8.1 Hz. The ^{13}C signal of $PC(CH_3)_3$ shifts



(1)

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† Dichloro[(8-methyl-2-quinolylmethyl)di-t-butylphosphine-*NP*]palladium(II).

TABLE 1

Proton n.m.r. data for mqp and eqp complexes; chemical shifts (δ), with ^{31}P couplings where relevant given in square brackets [a]

Compound	H^3	H^4	8-R	$PCH_2[^2J(P-H)/Hz]$	$PC(CH_3)_3[^3J(P-H)/Hz]$	Others [b]
mqp	7.49 (d)	7.96 (d)	2.75 (s)	3.26 (d) [3.5]	1.17 (d) [11.1]	(7.2—7.6)
[Me-mqp]I	8.13 (s)	8.13 (s)	2.70 (s)	4.43 (d) [13.9]	1.50 (d) [15.3]	(7.3—7.8); $P-CH_3$: 2.17 (d) [12.2]
eqp	7.51 (d)	7.96 (d)	3.30 (q), 1.40 (t)	3.25 (d) [3.8]	1.17 (d) [11.5]	(7.2—7.6)
Unidentate						
(1)	8.71 (d)	7.85 (d)	2.76 (s)	4.08 (t) [8.1] [c]	1.55 (t) [13.8] [d]	(7.2—7.8)
(7)	8.71 (d)	7.83 (d)	2.79 (s)	4.31 (t) [8.5] [c]	1.48 (t) [12.8] [d]	(7.2—7.8)
(8)	8.10 (d)	7.93 (d) [e]	2.78 (s)	3.97 (d) [12.6]	1.35 (d) [13.4]	(7.2—7.7); $COCH_3$: 1.77 (s) 2.14 (s), CH: 5.52 (s)
(4)	8.20 (d)	8.01 (d)	2.85 (s)	4.09 (d) [11.9]	1.38 (d) [13.8]	(7.1—7.6)
(3)	8.65 (d)	8.10 (d)	2.89 (s)	4.08 (d) [12.0]	1.58 (d) [13.5]	(7.1—7.8)
(14)	8.05 (s)	8.05 (s)	2.73 (s)	3.94 (d) [11.0]	1.59 (d) [13.0]	(7.1—7.8)
Bidentate						
(2)	*f*	7.88 (d)	3.87 (s)	3.92 (d) [g]	1.55 (d) [15.2]	(7.2—7.7)
(6)	*f*	8.08 (d)	3.60 (s)	3.89 (d) [8.2]	1.45 (d) [15.0]	(7.1—7.7)
(5)	7.80 (d)	8.24 (d)	3.34 (t) [h]	4.13 (d) [9.0]	1.47 (d) [14.7]	(7.2—7.8)
(15)	7.79 (d)	8.25 (d)	3.9 (m) [i]	4.17 (d) [9.5]	1.52 (d) [14.5]	(7.2—7.8)
Metallated						
(11)		8 00 (s)	2.75 (s)	3.55 (d) [10.5]	1.45 (d) [14.0]	(7.1—7.8)
(12)		*f*	2.70 (s)	3.31 (dd) [10.0], [j] 3.84 (dd) [10.0]	1.28 (d) [12.5] 1.12 (d) [12.5]	(7.0—8.1)
(13)		8.28 (s)	2.77 (s)	3.62 (d) [9.1]	1.33 (d) [13.0]	(7.1—7.7)

[a] Recorded at 100 MHz on a Varian HA100 spectrometer in $CDCl_3$ at 27 °C. [b] Values for H^{5-7} are in parentheses. [c] $(^2J + {}^4J)$ virtual coupling. [d] $(^3J + {}^5J)$ virtual coupling. [e] The H^3 and H^4 assignments could be reversed for these bracketed numbers. [f] Signal obscured by H^{5-7}. [g] Coupling obscured by 8-R signal. [h] Coupling 2.7 Hz. [i] Coupling to CH_2 too complex to be analysed, CH_3 obscured by $PC(CH_3)_3$. [j] $^2J(H-H)$ = 15.3 Hz.

TABLE 2

Carbon-13 n.m.r. shifts for new compounds [a]

	mqp and eqp resonances													
Compound	C^2 [b]	C^3 [c]	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	8-R	PCH_2 [d]	$PC(CH_3)_3$ [d]	$PC(CH_3)_3$ [b]	Other resonances
mqp	161.3 (d) (11.1)	121.8 (d) (7.7)	135.8	129.1	125.4	125.1	136.5	146.9	126.3	17.9	*e*	32.0 (d) (22.2)	29.6 (d) (13.3)	
eqp	161.4 (d) (11.3)	121.9 (d) (8.1)	136.2	127.7	125.4	125.4	142.4	147.0	126.5	15.3 24.3	*e*	32.1 (d) (19.7)	29.6 (d) (12.7)	
[Me-mqp]I	150.5 (d) (8.7)	121.9 (d) (5.1)	138.1	130.4	127.0	125.9	136.3	146.4	127.0	18.3	27.5 (d) (40.3)	34.5 (d) (37.2)	27.5 (s)	PCH_3: 2.6 (d) (46.9)
Unidentate														
(1)	156.6 (s)	123.8 (s)	135.2	129.3	125.8	125.4	136.8	147.1	126.9	18.1	*e*	38.4 (t) [f] (13.3)	30.8 (s)	
(7)	157.3 (s)	124.3 (s)	134.9	129.2	125.6	125.6	136.8	146.9	126.9	18.0	*e*	37.0 (t) [f] (15.6)	30.5 (s)	
(8)	157.0 (d) (1.5)	123.3 (s)	135.9	129.3	125.7	125.5	136.6	146.5	126.7	17.9	*e*	36.4 (d) (21.8)	29.9 (d) (2.9)	acac: CH, 101.0 (d) (1.5); CO, 184.4 (s), 188.6 (d) (1.4); CH_3, 29.2 (s), 29.4 (s)
(4)	156.6 (d) (1.2)	122.9 (d) (3.6)	136.4	130.3	126.2	125.7	137.2	146.6	127.1	18.8	*e*	36.4 (d) (17.2)	30.0 (d) (3.2)	
(3)	155.7 (d) (2.9)	123. 2 (s)	136.1	130.0	126.0	125.6	137.0	146.5	127.0	18.2	*e*	38.5 (d) (18.1)	30.4 (s)	
Bidentate														
(2)	161.5 (d) (3.2)	119.2 (d) (11.3)	140.5	134.4	128.0	126.4	136.8	147.2	128.2	23.9	38.5 (d) (24.3)	37.7 (d) (17.1)	29.0 (s)	
(6)	161.4 (d) (4.6)	119.4 (d) (9.7)	140.4	133.2	127.0	125.8	136.3	147.4	128.2	23.9	37.1 (d) (22.5)	35.5 (dd) [g] (21.5)	29.4 (d) (3.4)	Rh(CO): 191.6 (dd) (74.2, 21.1)
(5)	163.5 (d) (2.4)	120.9 (d) (10.6)	141.2	133.7	127.3	126.9	134.0	146.9	128.1	14.3 (dd) [h]	38.5 (d) (24.6)	37.0 (dd) [i] (22.3)	29.5 (d) (2.8)	Rh(CO): 181.1 (d) (73.5) 189.8 (dd) (72.4, 20.1)
(15)	163.9 (d) (1.8)	121.2 (d) (10.9)	141.4	130.8	127.4	126.9	139.6	146.3	127.9	15.0 (s), 19.8 (m) [j]	38.5 (d) (23.8)	37.0 (dd) [k] (22.3)	29.5 (d) (2.4)	Rh(CO): 180.9 (d) (72.9) 189.7 (dd) (72.5, 20.1)
Metallated														
(10)	156.9 (d) (2.5)	125.0 (d) (4.1)	135.8	129.5	125.9	125.4	136.7	146.9	126.9	18.3	*e*	39.7 (d) (12.2)	31.4 (s)	

[a] Recorded at 23 °C in $CDCl_3$ on a Varian CFT20 spectrometer. *J* in Hz. Assignments of the signals for C^{5-7} may be permuted. [b] $^2J(P-C)$ in parentheses. [c] $^3J(P-C$ in parentheses. [d] $^1J(P-C)$ in parentheses. [e] Obscured by $PC(CH_3)_3$ resonance. [f] ^1J- + ^3J-(P–C) in parentheses. [g] $^2J(Rh-C)$ = 20. Hz. [h] Couplings = 6.7 and 2.4 Hz. [i] $^2J(Rh-C)$ = 2.7 H2. [j] $8-CH_2CH_3$ multiplet not resolved. [k] $^2J(Rh-C)$ = 2.1 Hz.

downfield by 6.5 p.p.m. while the ^{31}P coupling to PC(CH_3)$_3$ drops from 13.3 to 0 Hz.

When only 1 equivalent of mqp was added to a solution of $Na_2[PdCl_4]$ in methanol an orange precipitate analysing as $[PdCl_2(mqp)]$, (2), was immediately formed, and recrystallised from CH_2Cl_2–Et_2O as $[PdCl_2(mqp)]\cdot x$ CH_2Cl_2 where x varies from 0 to 1. Proton and ^{13}C n.m.r. spectra (Tables 1 and 2) indicate that (2) is not a simple chloro-bridged dimer as with other tertiary phosphines since it contains bidentate mqp as shown by the large co-ordination shifts of the 8-Me resonances. The 8-CH_3 signal shifts 1.12 p.p.m. downfield relative to the free ligand, while the 8-CH_3 signal appears at δ 23.9, a shift of −6.0 p.p.m. The only other shift characterising bidentate co-ordination is that of PCH_2. For free and unidentate mqp this signal is at δ *ca.* 29.6 and is obscured by the intense PC(CH_3)$_3$ resonance. However, on chelation through the quinoline nitrogen atom as in (2) it shifts by 8.7 p.p.m. to δ 38.5. This shift is attributed to the presence of the five-membered metallocycle through this atom. The preparation of the monodeuteriated ligand $C_{10}NH_8(CHD-PBu^t_2)$ helped with this assignment. We have described our n.m.r. criteria for the mode of mqp co-ordination as these were applied to other complexes in this paper and these will not be given again.

TABLE 3

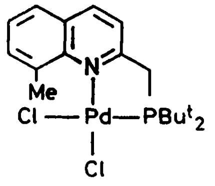
Infrared data (cm^{-1}) for mqp and eqp complexes

	Compound	ν(CO) [a]
(5)	$[Rh_2Cl_2(CO)_3(mqp)]$	1 985, 2 003, 2 074
(15)	$[Rh_2Cl_2(CO)_3(eqp)]$	1 985, 2 003, 2 075
(6)	$[RhCl(CO)(mqp)]$	1 986
(7)	$[RhCl(CO)(mqp)_2]$	1 954br
(8)	$[Rh(acac)(CO)(mqp)]$	1 975
(4)	$[RhCl(CO)_2(mqp)]$	1 996, 2 089
(13)	$[Mn(mqp-H^3)(CO)_4]$	2 058, 1 980, 1 971, 1 947
(14)	$[MnBr(CO)_4(mqp)]$	2 083, 2 014, 2 003, 1 946
		ν(M–Cl) [b]
(1)	$[PdCl_2(mqp)_2]$	345.5
(2)	$[PdCl_2(mqp)]$	324.5, 275
(5)	$[Rh_2Cl_2(CO)_3(mqp)]$	315, 286
(6)	$[RhCl(CO)(mqp)]$	280.5
(7)	$[RhCl(CO)(mqp)_2]$	289
(9)	$[\{PdCl(mqp-H^3)\cdot HCl\}_2]$	280, 259
(10)	$[\{PdCl(mqp-H^3)\}_2]$	279, 255
		ν(Ir–H) [b]
(12)	$[IrH(Cl)(mqp-H^3)(NC_5D_5)_2]$	2 180

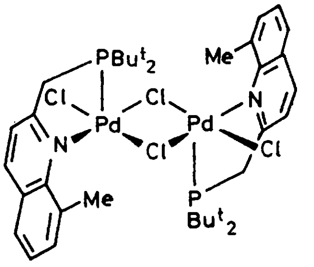
[a] In cyclohexane solution. [b] Nujol mulls.

Two structures (2a) and (2b) were considered and we favoured (2b) initially. It would seem for simple steric reasons that the mqp ligand in (2b) must lie perpendicular to the square plane with the P atom in an axial site so that the 8-Me group is in the vacant sixth one. Mononuclear (2a) with mqp lying in the co-ordination plane seemed to imply a prohibitive clash between the 8-Me group and the Cl ligand *trans* to P, and it is also difficult to see how the very large downfield shifts observed from the 8-CH_3 signals could arise. Such shifts are only found when the alkyl group occupies space *above* the co-ordination plane. To resolve the matter a single-crystal *X*-ray determination was carried out which showed that the complex adopts form (2a) but with distortions such as to drastically reduce the 8-Me ··· Pd and 8-Me ··· Cl interactions.

Figure 1 shows the molecular structure (with the labelling scheme) as determined for a sample of (2) which analysed as $[PdCl_2(mqp)]\cdot 0.8CH_2Cl_2$. The dichloromethane molecules are severely disordered, occupy open regions in the crystal, and show no significantly close approach to the complex. Important interatomic distances and interbond angles are given in Table 4 while selected least-square planes and dihedral angles are presented in Table 5. Complete lists are given in the Supplementary Publication (see below).



(2a)



(2b)

The square-planar arrangement about Pd is distorted with what is best considered as the movement of Cl(1) out of the plane defined by the PdNPCl(2) atoms by 0.66 Å. This displacement seems to be caused by the repulsion of the 8-Me group which is situated above Cl(1) with the distance Cl(1)–C(11) 3.311 Å. The mutually *cis* Cl atoms have normal bond lengths: Pd–Cl(1) 2.393 and Pd–Cl(2) 2.294 Å. The longer bond to Cl(1) reflects the larger *trans* influence of P over N. The Pd–N distances are also normal. In order to achieve the relatively long distances of C(11) from Cl(1) and Pd (3.311 and 3.128 Å

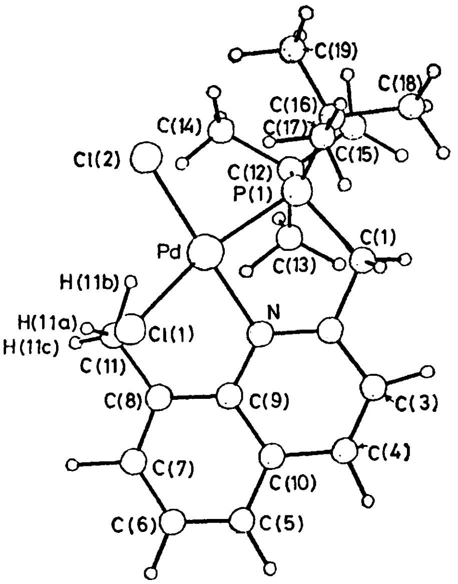


FIGURE 1 Structure of $[PdCl_2(mqp)]$, (2), showing the atom-numbering scheme. All hydrogen atoms are shown but only those on C(11) are numbered

TABLE 4

Important interatomic distances (Å) and angles (°) (estimated standard deviations in parentheses)

(*a*) Lengths

Pd–Cl(1)	2.393(1)	Pd–Cl(2)	2.294(1)
Pd–P(1)	2.229(1)	Pd–N(1)	2.078(4)
P(1)–C(12)	1.867(5)	P(1)–C(16)	1.871(5)
P(1)–C(1)	1.838(6)	C(11)–C(8)	1.497(8)
C(1)–C(2)	1.490(7)	C(8)–C(9)	1.423(7)
C(2)–N(1)	1.339(6)	C(9)–N(1)	1.396(9)
C(2)–C(3)	1.388(9)	C(3)–C(4)	1.360(9)
C(4)–C(10)	1.419(8)	C(10)–C(5)	1.402(9)
C(5)–C(6)	1.367(10)	C(6)–C(7)	1.384(10)
C(7)–C(8)	1.370(8)	C(9)–C(10)	1.418(8)

(*b*) Selected non-bonded intramolecular contacts

Pd · · · C(11)	3.128	Pd · · · H(11b)	2.492
Cl(1) · · · C(11)	3.311	Cl(1) · · · H(11a)	2.444

(*c*) Interbond angles

Cl(1)–Pd–Cl(2)	90.8(1)	Cl(1)–Pd–P(1)	164.9(1)
Cl(1)–Pd–N(1)	92.6(1)	Cl(2)–Pd–P(1)	95.0(1)
Cl(2)–Pd–N(1)	176.0(1)	P(1)–Pd–N(1)	82.3(1)
Pd–N(1)–C(2)	114.7(3)	Pd–N(1)–C(9)	125.0(3)
C(9)–C(8)–C(11)	124.2(4)	C(7)–C(8)–C(11)	118.3(5)
C(7)–C(8)–C(9)	117.1(5)		

respectively), the chelate has had to undergo a number of distortions from a planar arrangement. The first may be considered as a rotation about the Pd–N bond by 43°. Although this will not reduce the 8-Me · · · Pd interaction, it drastically increases the C(11)–Cl(1) distance. The second is a small pyramidal distortion at the nitrogen atom (sum of three bond angles = 259.0°) similar to but smaller than those seen in $[\mathrm{Pd}(\eta\text{-}C_3H_5)L]^+$ (L = 8-isopropylquinoline-2-carboxaldehyde-*N*-methylimine [1] or 8,8′-dimethyl-2,2′-biquinolyl [6]). This increases both the C(11)–Pd and C(11)–Cl(1) distances. A third distortion involves a buckling of the quinoline rings in order to reduce the C(11)–Pd repulsion and is best described by the torsional angles C(2)NC(9)C(8) 17.4 and NC(9)C(8)-C(11) 8.4°. The overall result of the pyramidal distortion and the buckling of the quinoline rings is that the N–Pd and C(8)–C(11) bonds which would be coplanar in an undistorted structure (such as for unidentate 8-methylquinoline) now lie at an angle of 37.0°. Figure 2 shows better than Figure 1 the position of the quinoline ligand with respect to the co-ordination plane and the non-planarity of the chelate ring with C(1) and C(2) out of the co-ordination plane.

TABLE 5

Selected least-squares planes in the form $Ax + By + Cz = D$, where x,y,z are fractional co-ordinates. Deviations (Å × 10^3) of relevant atoms are given in square brackets

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

$$-8.265x + 8.730y + 7.463z = 1.540$$

[Cl(1) 587, Cl(2) −120, C(1) 1 020, C(2) 741, C(3) 1 208, C(4) 920, C(5) −388, C(6) −1 369, C(7) −1 951, C(8) 1 560, C(9) −500, C(10) 25, C(11) −2 370]

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

$$-8.164x + 8.991y + 7.106z = 1.513$$

[Pd 38, Cl(1) 658, Cl(2) −19, P(1) 1, C(1) 977, N(1) −21, C(2) 691, C(3) 1 122, C(4) 828, C(5) −462, C(6) −1 418, C(7) −1 968, C(8) −1 566, C(9) −525, C(10) −39, C(11) −2 344]

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

$$8.045x - 9.721y + 2.025z = 0.916$$

[Pd −753, Cl(1) −2 438, Cl(2) −1.355, P(1) 473, C(1) 156, N(1) −70, C(2) 20, C(3) 42, C(4) −49, C(5) 48, C(6) 248, C(7) 422, C(8) 338, C(9) 61, C(10) −3, C(11) 692]

Plane (4): C(5)—C(10)

$$7.353x - 9.404y + 4.415z = 1.475$$

[Pd −909, Cl(1) −2 761, Cl(2) 1 680, P(1) 552, C(1) 455, N(1) −75, C(2) 229, C(3) 390, C(4) 216, C(5) −4, C(6) −24, C(7) 20, C(8) 12, C(9) −39, C(10) 35, C(11) 210]

Angles (°) between normals to planes:

(1)—(2)	1.8	(2)—(3)	144.1
(1)—(3)	142.6	(2)—(4)	134.8
(1)—(4)	133.3	(3)—(4)	9.3

(*b*) 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

P(1)–C(1)–C(2)–N(1)	−10.2
Pd–N(1)–C(2)–C(1)	−24.0
C(9)–N(1)–C(2)–C(1)	167.7
C(2)–N(1)–C(9)–C(8)	−162.6
C(11)–C(8)–C(9)–N(1)	8.4

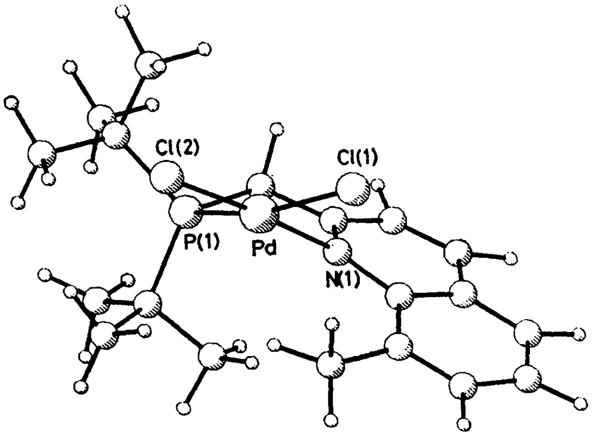
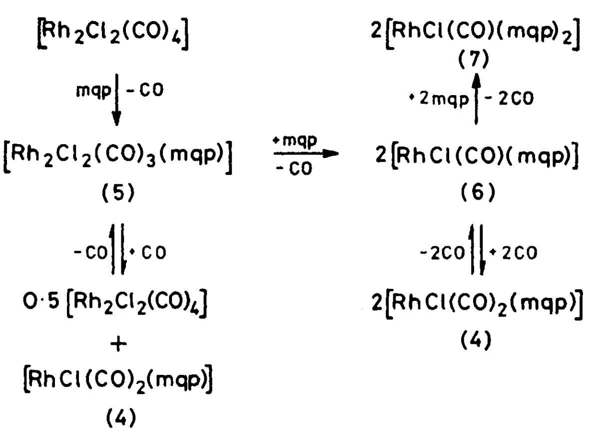


FIGURE 2 Structure of (2) showing ligand displacements out of the co-ordination plane and the non-planarity of the chelate ring

Perhaps as expected from the strained nature of this chelation the quinoline nitrogen atom in (2) is readily displaced by mqp to give complex (1) or by pyridine to give $[\mathrm{PdCl_2(mqp)(py)}]$, (3). The i.r. and ^{1}H and ^{13}C n.m.r. spectra of (3) are consistent with unidentate mqp and *trans*-chloride ligands. An interesting feature of (2) is the observation of single n.m.r. resonances for the $\mathrm{PC}H_2$ and $\mathrm{PC(C}H_3)_3$ nuclei in spite of the non-planar chelate ring. A rapid dynamic process involves effective rotation of the quinoline group through the co-ordination plane so that a time-averaged plane of symmetry lies through the chelate ring. We doubt if a simple rotation could occur because of the 8Me · · · Cl clash, but believe rather that there is a unidentate mqp intermediate complex, possibly $[\mathrm{(mqp)ClPd(\mu\text{-}Cl)_2PdCl(mqp)}]$, but we have not studied this process mechanistically.

Rhodium(I) *Complexes of mqp*.—The application of i.r. and ^{1}H n.m.r. spectrometry, gasometry, *etc.* to a study of the reactions of $[\mathrm{Rh_2Cl_2(CO)_4}]$ with unidentate phosphines has shown that various products are formed depending upon the ratio of ligand to metal and whether the reaction is carried out under CO or an inert atmosphere.[7-9] The reaction with mqp is similar and complexes (4)—(7) are formed under various conditions (see Scheme 1). Proton, ^{13}C, and ^{31}P n.m.r. data are given in Tables 1, 2, and 6. These spectra indicate that *trans*-[RhCl(CO)(mqp)$_2$], (7), contains two mutually *trans*-unidentate mqp ligands, so that it is analogous to (1). Shaw and his co-workers[10] have shown that the size of the co-ordination shifts in the ^{31}P n.m.r. spectra of *trans*-[RhCl(CO)L$_2$] correlate with the cone angle of the phosphine L.



SCHEME 1 Formation of rhodium(I) complexes (4)—(7)

Using our observed shift of -24.7 p.p.m. between the ^{31}P resonances of the free ligand and that co-ordinated in (7) (Table 6), the cone angle of mqp in this complex is 166 ± 3°, very similar to that (172°) of PBu$^t_2$(CH$_2$Ph) as calculated by Tolman,[11] showing the structural similarity of unidentate mqp to this ligand.

On adding only one mqp molecule per Rh atom to a solution of [Rh$_2$Cl(CO)$_4$] in light petroleum under CO, the i.r. spectrum shows the presence of *cis*-[RhCl(CO)$_2$(mqp)] (4). However, this complex readily loses CO and attempts to isolate it gave the slightly soluble complex [RhCl(CO)(mqp)], (6) (see Scheme 1). Proton and ^{13}C n.m.r. shifts for this complex are remarkably similar to those seen for (2) so we have assigned it the analogous structure shown. The CO ligand gave a doublet of doublets [^1J(Rh–C) = 74.2 and ^2J(P–C) = 21.2 Hz] in the ^{13}C n.m.r. spectrum consistent with it being *cis* to the P atom. The i.r. spectra of the stoicheiometrically equivalent [Rh$_2$Cl$_2$(CO)$_2$L$_2$] (L = PMe$_3$, PMe$_2$Ph, or PPh$_3$) are different from that of (6). The ν(CO) absorptions for these dimers in the range 1 979—1 980 cm^{-1} are insensitive to the ligand,[7] while (6) has an absorption at 1 986 cm^{-1}. The compound [RhCl(CO)(PPh$_3$)(py)][8] is formally related to (6) except that the pyridine is *trans* to P not *cis* as it must be for complete analogy with (6).

TABLE 6

Phosphorus-31 n.m.r. data*

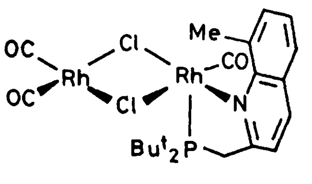
	Compound	δ	^1J(Rh–P)/Hz
	mqp	-35.89 (s)	
	[Me-mqp]I	-48.18 (s)	
	eqp	-34.74 (s)	
(1)	[PdCl$_2$(mqp)$_2$]	-45.97 (s)	
(2)	[PdCl$_2$(mqp)]	-86.92 (s)	
(5)	[Rh$_2$Cl$_2$(CO)$_3$(mqp)]	-104.65 (d)	185.0
(15)	[Rh$_2$Cl$_2$(CO)$_3$(eqp)]	-104.64 (d)	188.2
(6)	[RhCl(CO)(mqp)]	-98.05 (d)	166.5
(7)	[RhCl(CO)(mqp)$_2$]	-60.60 (d)	119.6
(8)	[Rh(acac)(CO)(mqp)]	-83.14 (d)	171.2

* Measured at 32.19 MHz on a Varian CFT20 spectrometer at 23 °C in CDCl$_3$, relative to external 85% H$_3$PO$_4$. All spectra were recorded with proton decoupling.

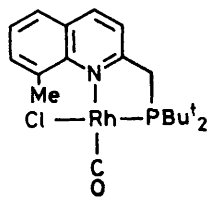
Solutions of (6) show immediate differences in their ^{1}H n.m.r. spectra on reaction with CO, consistent with a change from bi- to uni-dentate bonding. The 8-C*H*$_3$ signal moves upfield from δ 3.60 in (6) to δ 2.85 as the amount of CO added is increased. This final figure, when the atmosphere is pure CO, seems to correspond to almost complete conversion into (4). The single set of signals at intermediate CO concentrations is due to averaging of signals of (4) and (6) by the rapid equilibrium shown in Scheme 1. Even under an atmosphere of pure CO, however, there is some (6) present as the ^{31}P-{^{1}H} n.m.r. spectrum (23 °C) shows a broad hump rather than a sharp doublet.

Addition of 1 equivalent of mqp to solutions of [Rh(acac)(CO)$_2$] (acac = pentane-2,4-dionate) gave the stable complex [Rh(acac)(CO)(mqp)], (8), containing unidentate mqp and with n.m.r. spectra very like those of complex (4) above.

Complex (5), [Rh$_2$Cl$_2$(CO)$_3$(mqp)], is the most interesting to be isolated in this work. It is obtained as a yellow powder when only half a molecule of mqp per Rh atom was added to a light petroleum solution of [Rh$_2$Cl$_2$(CO)$_4$] through which a steady stream of N$_2$ was bubbled. Complexes of the same stoicheiometry with unidentate phosphines (PMe$_3$, PMe$_2$Ph, or PPh$_3$) are binuclear with chloro-bridges.[7] The ν(CO) spectrum (in C$_6$H$_{12}$) of (5) is consistent with this type of structure with absorptions at 2 075, 2 003, and 1 985 cm^{-1} showing that (5) is not a mixture of [Rh$_2$Cl$_2$(CO)$_4$] and [RhCl(CO)(mqp)], (6) (Table 3). The ν(Rh–Cl) absorptions at 315 and 286 cm^{-1} are also consistent with a chloro-bridged structure. The ν(CO) spectrum of a CO-saturated cyclohexane solution shows this to contain a mixture of [Rh$_2$Cl$_2$(CO)$_4$] and [RhCl(CO)$_2$(mqp)], (4). These observations are all consistent with the formulation [(OC)$_2$Rh(μ-Cl)$_2$Rh(CO)(mqp)] for (5).



(5)



(6)

Proton and ^{13}C n.m.r. spectra of (5) (Tables 1 and 2 and Figure 3) show bidentate mqp so that the phosphine-bound rhodium is five-co-ordinate, but there are some unique features to these spectra. Thus the 8-C*H*$_3$ signal is shifted downfield by 0.59 p.p.m. and is a triplet (*J* = 2.7 Hz; Figure 3), while the ^{13}C-{^{1}H} n.m.r. signal for this group is shifted upfield by 3.6 p.p.m. appearing as a doublet of doublets (*J* = 6.7 and 2.3 Hz). Decoupler offset experiments rule out C–H cleavage since the 8-*C*H$_3$ nucleus couples equally to three H nuclei in addition

TABLE 7

Analytical data (%) with calculated values in parentheses

	Compound	C	H	N	Cl or Br	P
(1)	$[PdCl_2(mqp)_2]$	58.15 (58.5)	7.15 (7.25)	3.50 (3.60)	9.20 (9.10)	7.55 (7.95)
(2)	$[PdCl_2(mqp)]$	47.15 (47.65)	6.00 (5.80)	2.70 (2.95)	14.85 (14.8)	6.80 (6.50)
(2)	$[PdCl_2(mqp)]\cdot 0.8CH_2Cl_2$	43.6 (43.5)	5.75 (5.45)	2.45 (2.55)	23.35 (23.35)	5.95 (5.65)
(3)	$[PdCl_2(mqp)(py)]$	51.8 (51.7)	5.95 (5.95)	4.80 (5.00)	13.1 (12.7)	5.65 (5.55)
(5)	$[Rh_2Cl_2(CO)_3(mqp)]$	41.6 (39.9)	4.60 (4.25)	2.35 (2.10)	10.7 (10.7)	5.55 (4.70)
(6)	$[RhCl(CO)(mqp)]$	51.5 (51.35)	6.35 (6.05)	2.60 (3.00)	7.75 (7.60)	6.65 (6.60)
(7)	$[RhCl(CO)(mqp)_2]$	60.25 (60.9)	7.50 (7.35)	3.45 (3.65)	5.60 (4.60)	8.30 (8.05)
(8)	$[Rh(acac)(CO)(mqp)]$	56.8 (56.5)	7.00 (6.65)	2.50 (2.65)		6.15 (5.80)
(9)	$[\{PdCl(mqp-H^3)\cdot HCl\}_2]$	47.0 (47.65)	5.80 (5.80)	2.60 (2.95)	15.7 (14.8)	6.70 (6.50)
(10)	$[\{PdCl(mqp-H^3)\}_2]$	50.9 (51.6)	6.15 (6.15)	3.15 (3.15)	8.30 (8.00)	7.40 (7.00)
(11)	$[PdCl(mqp-H^3)(py)]$	54.7 (54.75)	6.10 (6.15)	5.45 (5.30)	6.80 (6.75)	5.95 (5.85)
(12)	$[IrH(Cl)(mqp-H^3)(NC_5D_5)_2]$	49.1 (49.95)	5.65 (5.50)	5.95 (6.05)	5.50 (5.10)	4.90 (4.45)
(13)	$[Mn(mqp-H^3)(CO)_4]$	59.2 (59.1)	6.05 (5.80)	2.95 (3.00)		6.60 (6.65)
(14)	$[MnBr(CO)_4(mqp)]$	50.45 (50.4)	5.30 (5.15)	2.55 (2.55)	14.4 (14.55)	5.65 (5.65)

to the above non-proton couplings. The chemical shifts of other signals are very similar to those of (2) and (6) showing that mqp is chelated. We believe that an 8-alkyl–metal interaction gives rise to coupling between both the ^{31}P and one ^{103}Rh nucleus and the 8-CH_3 group. The alternative, with coupling involving two non-equivalent ^{103}Rh nuclei, is difficult to reconcile with the necessary lack of coupling to ^{31}P. We interpret this result in terms of the arrangement in Scheme 2 with sufficient electron density between the Rh atom and the CH_3 group. A rapid rotation about the 8-CH_3-C bond averages the coupling over H^a, H^b, and H^c and to obtain a triplet $^1J(Rh-H) = {}^2J(P-H)$. The $^{31}P-\{^1H\}$ n.m.r. spectrum is a simple doublet [$^1J(Rh-P) = 185$ Hz] and without ^1H decoupling the signal is too complex for analysis so that coupling to the 8-Me group could not be identified.

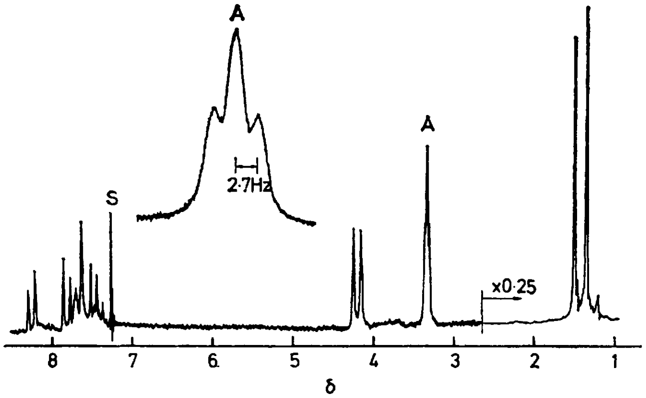
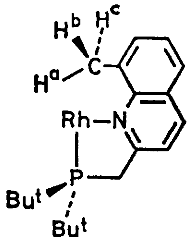


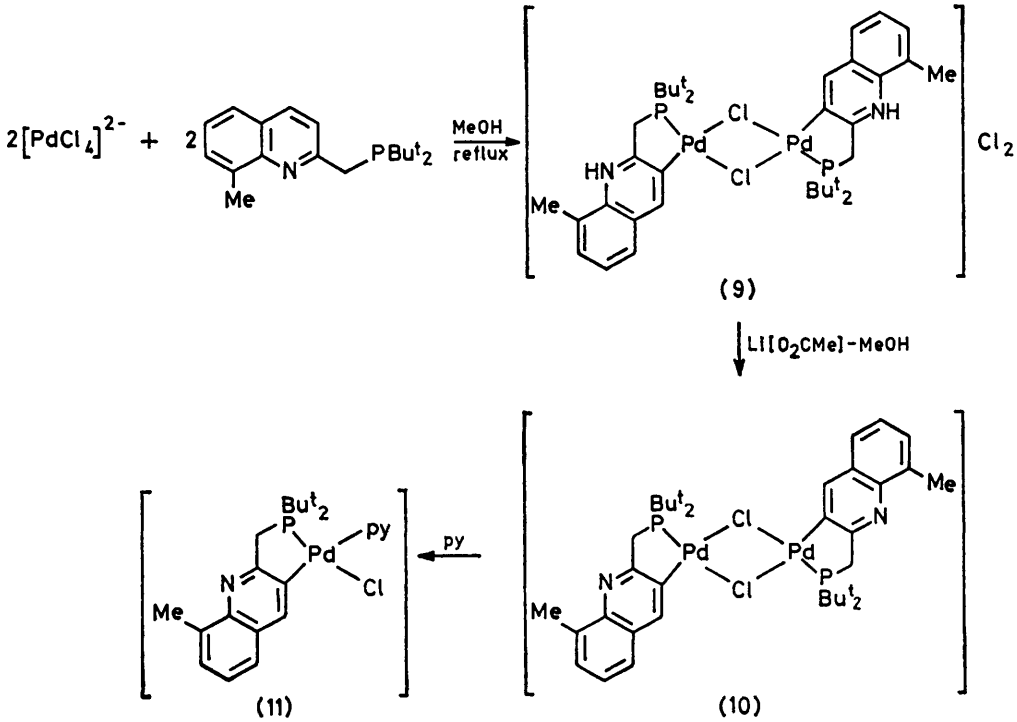
FIGURE 3 Proton n.m.r. spectrum of $[Rh_2Cl_2(CO)_3(mqp)]$, (5), showing an expansion of the triplet pattern A for the 8-methyl group (S = $CHCl_3$ in $CDCl_3$)

Crystals of (5) suitable for *X*-ray determination were not obtained because it readily decomposed in solution even under N_2, and even the solid powder darkened to dark brown at room temperature. Reprecipitating from $CHCl_3$ by adding light petroleum gave a deep red oil eventually solidifying to a dark impure mass. Thus the geometric nature of the $CH_3\cdots Rh$ interaction is unknown, but it is possible that the CH_3 group occupies the sixth co-ordination site of a five-co-ordinate Rh atom. The structure shown is only one possibility. In this or in any other related structure, the PCH_2 and $PC(CH_3)_3$ protons should be diastereotopic and give an AB quartet of doublets and a pair of doublets in the ^1H n.m.r., but single resonances only were observed even at −65 °C implying that a rapid process generates a time-averaged plane of symmetry through the ligand.



SCHEME 2

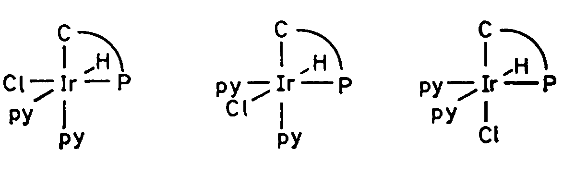
The corresponding 8-Et complex $[Rh_2Cl_2(CO)_3(eqp)]$, (15), shows very similar ^1H n.m.r. effects as the 8-Me complex (5). The 8-CH_2CH_2 protons show coupling to nuclei other than the CH_3CH_2 protons, but the observed multiplet was insufficiently resolved for satisfactory analysis. The CH_3CH_2 n.m.r. signal is shifted upfield as is the corresponding signal for (5), but coupling to ^{103}Rh and ^{31}P leading to signal broadening was not resolved. The expected diastereotopic nature of the $8\text{-}CH_3CH_2$ protons is not detected presumably for the same reasons that separated PCH_2 and $PC(CH_3)_3$ signals were not observed.



Scheme 3

Metallation Reactions of mqp.—The only cyclometallated complexes of mqp observed were those resulting from 3-H bond cleavage; no $8\text{-}CH_3$ metallation occurred. Treatment of mqp with palladium(II) acetate (which gave total 8-metallation with the corresponding imine mqa[1]) gave only intractable black oils, but the reaction of mqp with $Na_2[PdCl_4]$ (1 mol per mol Pd) in refluxing methanol gave a very insoluble grey precipitate which analyses as $[PdCl_2(mqp)]$, (9), but which is different from (2). On stirring a suspension of (9) with $Li[O_2CMe]$ in methanol for 5 min a new product identified as $[Pd_2Cl_2(mqp-H^3)_2]$, (10), was obtained. Both (9) and (10) are too insoluble for n.m.r. identification, but (10) reacts with pyridine to give the very soluble complex $[PdCl(mqp-H^3)(py)]$, (11). An authentic sample of (10) was also obtained by heating $[PdCl_2(mqp)]$, (2), in 2-methoxyethanol with $Li[O_2CMe]$. The structures of (9) and (10) are believed to be as shown in Scheme 3. The far i.r. spectra of these complexes are very similar with two ν(Pd–Cl) absorptions at 280,259 and 279,255 cm^{-1} respectively. These positions are very close to those reported for the chloro-bridged dimer formed by cyclopalladation of $PBu^t_2(CH_2Ph)$ (280,252 cm^{-1}).[5] Compound (9) is produced by protonation of the quinoline nitrogen atom with HCl generated in the metallation reaction, but in the presence of acetate ions compound (10) and acetic acid are formed.

The ligand mqp was found to undergo oxidative addition at the 3 position even more readily than the corresponding imine mqa. Thus on warming a mixture of $[Ir_2Cl_2(C_8H_{14})_4]$ (C_8H_{14} = cyclo-octene), mqp, and $[^2H_5]$pyridine in hexane, a pale precipitate of $[IrH(Cl)(mqp-H^3)(NC_5D_5)_2]$, (12), was formed. The Ir–H group was easily identified [ν(Ir–H) at 2 180 cm^{-1} and a ^1H n.m.r. doublet at δ – 22.73 with ^2J(P–H) indicating these ligands are mutually *cis*]. There is no plane of symmetry through the chelate since a pair of ^1H n.m.r. doublets for $PC(CH_3)$ and an AB quartet of doublets for PCH_2 protons are observed. Compound (12) is one of three possible isomers, assuming that CH addition is *cis* (Scheme 4). Analogous complexes have been obtained using $PBu^t_2(CH_2Ph)$.[12]



Scheme 4

The compound $[Mn(CH_3)(CO)_5]$ has been well studied as a metallating agent for N and P donor ligands with the hydrogen atom being lost with CH_3 as methane.[13] On refluxing a mixture of $[Mn(CH_3)(CO)_5]$ and mqp in cyclohexane, the complex $[Mn(mqp - H^3)(CO)_4]$, (**13**), was obtained and identified by ^1H n.m.r. spectroscopy. An intermediate unmetallated complex containing unidentate mqp was not observed on monitoring the reacting solution by its i.r. spectrum, but when $[MnBr(CO)_5]$ was used the complex $[MnBr(CO)_4(mqp)]$, (**14**), containing unidentate mqp was obtained.

EXPERIMENTAL

Synthesis of mqp.—The whole procedure, work-up, and handling requires oxygen-free conditions. 2,8-Dimethylquinoline (1.0 g, 6.4 mmol) in diethyl ether (5 cm^3) was added to a solution of LiBu (6.5 mmol) in ether (20 cm^3) at room temperature to give a dark red solution of 8-methyl-2-quinolylmethyl-lithium with butane evolution. The formation of this lithium reagent was confirmed separately by hydrolysis with D_2O to give the original dimethylquinoline mono-deuteriated at the 2-methyl group. The red solution was added slowly after 5 min to a solution of PBu^t_2Cl (1.15 g, 6.4 mmol) in ether (20 cm^3) at 0 °C. The red colour was discharged and the resulting suspension refluxed for 30 min and then hydrolysed with deaerated water. Work-up gave the crude product as a very viscous yellow oil (1.7 g, 90%). Complete purification proved impossible; the oil was very soluble in common solvents and could not be crystallised. Attempted distillation gave only 2,8-dimethylquinoline and mass spectroscopy showed no parent molecular ion, but one due to loss of C_4H_{10} from this. The crude oil was taken up in pentane, the phosphine oxide impurity filtered off, and the oil reformed by evaporation.

A gravimetric determination involved reaction of the phosphine with MeI in acetone (30 min) and addition of ether to give the methylphosphonium iodide of mqp as a white crystalline solid in yields indicating a purity of 80—90% for the parent phosphine (Found: C, 53.85; H, 7.05; I, 28.55; N, 3.15; P, 6.8. $C_{20}H_{31}INP$ requires C, 54.2; H, 7.05; I, 28.6; N, 3.15; P, 7.0%). The remaining organic residue was found to be mainly 2,8-dimethylquinoline (^1H n.m.r.).

The corresponding 8-ethyl analogue (eqp) was obtained similarly.

Preparation of $[PdCl_2(mqp)_2]$, (1).—The compound mqp (0.20 g, 2 mol per mol Pd) was added to a solution of $Na_2[PdCl_4]$ (0.10 g) in methanol (5 cm^3). The deep red colour of the solution was immediately discharged to give a light yellow solution which deposited a yellow powder over 10 min. Recrystallisation from $CHCl_3$ by adding diethyl ether gave yellow *crystals* of the product (0.19 g, 74%).

Preparation of $[PdCl_2(mqp)]$, (2).—By a similar method but using half as much mqp (0.10 g), an orange precipitate of (2) was rapidly obtained (0.14 g, 88%). Recrystallisation from CH_2Cl_2 by adding diethyl ether gave deep orange *crystals* containing various amounts of occluded CH_2Cl_2 solvent. The sample used for *X*-ray crystallography analysed as $[PdCl_2(mqp)]\cdot 0.8CH_2Cl_2$. Addition of an excess of pyridine to a chloroform solution of (2) followed by diethyl ether gave $[PdCl_2(mqp)(py)]$ (3) as pale yellow *microcrystals*.

Palladation of mqp.—(*a*) A mixture of $Na_2[PdCl_4]$ (0.3 g) in methanol (30 cm^3) was refluxed for 12 h. A grey *precipitate* formed was filtered off and washed with methanol and diethyl ether to give $[\{PdCl(mqp - H^3)\cdot HCl\}_2]$, (9) (0.3 g, 63%). This was insoluble in methanol and chloroform, but on warming a suspension with lithium acetate in methanol, pale yellow crystals of $[\{PdCl(mqp - H^3)\}_2]$, (10), were obtained.

(*b*) A mixture of complex (2) (0.5 g) and lithium acetate (0.2 g) in 2-methoxyethanol (15 cm^3) was refluxed for 1.5 h. The solution was filtered while hot to remove some Pd metal and the solvent removed under vacuum. Addition of methanol and cooling gave pale yellow *crystals* of complex (10) (0.28 g, 61%).

Addition of an excess of pyridine to a chloroform solution of complex (10) followed by diethyl ether gave $[PdCl(mqp - H^3)(py)]$, (11), as a white *solid.*

Preparation of $[RhCl(CO)(mqp)_2]$, (7).—The compound mqp (0.31 g, 2 mol per mol Rh atoms) was added to a solution of $[Rh_2Cl_2(CO)_4]$ (0.1 g) in chloroform (10 cm^3). Carbon monoxide was evolved and after removal of the solvent the residual oil was taken up in light petroleum (b.p. 40—60 °C) and cooled to give the product as yellow *crystals* (0.29 g, 73%).

Preparation of $[RhCl(CO)(mqp)]$, (6).—(*a*) On mixing equimolar amounts of (7) (0.20 g) and $[Rh_2Cl_2(CO)_4]$ (0.06 g) in light petroleum (b.p. 40—60 °C; 20 cm^3) and refluxing for 15 min, a pale yellow *precipitate* of the product was formed (0.12 g, 93%).

(*b*) The compound mqp (0.31 g) was added to a solution of $[Rh_2Cl_2(CO)_4]$ (0.2 g) in light petroleum (b.p. 40—60 °C; 20 cm^3) and the mixture refluxed for 15 min. On cooling the product was obtained as a pale yellow *powder* (0.36 g, 75%).

On bubbling CO through a suspension of (6) in light petroleum (b.p. 40—60 °C) a clear yellow solution of $[RhCl(CO)_2(mqp)]$, (4), was formed. However, only (6) could be isolated from such solutions.

Preparation of $[Rh_2Cl_2(CO)_3(mqp)]$, (5).—A steady stream of N_2 was passed through a solution of $[Rh_2Cl_2(CO)_4]$ (0.48 g) in light petroleum (30 cm^3) while a solution of mqp (0.40 g) in the same solvent (3 cm^3) was slowly added. An immediate pale yellow *precipitate* formed and was washed with pentane and dried under vacuum (0.46 g, 60%). Similar yields of the corresponding eqp complex were also obtained.

Preparation of $[Rh(acac)(CO)(mqp)]$, (8).—The compound mqp (0.6 g) was added to a solution of $[Rh(acac)(CO)_2]$ (0.51 g) in chloroform (20 cm^3). Carbon monoxide was evolved and the solution became dark yellow. Removal of the solvent followed by addition of light petroleum gave the product as yellow *needles* (0.9 g, 85%).

Preparation of $[IrH(Cl)(mqp - H^3)(NC_5D_5)_2]$, (12).—A suspension of $[Ir_2Cl_2(C_8H_{14})_4]$ (C_8H_{14} = cyclo-octene; 0.66 g) and perdeuteriopyridine (0.2 g, excess) in hexane (20 cm^3) was stirred to give a clear solution. The compound mqp (0.45 g) was added and the mixture heated at 50 °C for 30 min. A pale yellow *precipitate* was formed and, after cooling to −15 °C, was filtered off and washed with hexane (0.81 g, 78%).

Preparation of $[MnBr(CO)_4(mqp)]$, (14).—A mixture of $[MnBr(CO)_5]$ (0.28 g) and mqp (0.30 g) in light petroleum (b.p. 40—60 °C; 40 cm^3) was refluxed for 1 h and cooled to −15 °C to give large orange-red *crystals* of product (0.44 g, 80%).

Preparation of $[Mn(mqp - H^3)(CO)_4]$, (13).—A mixture of $[Mn(CH_3)(CO)_5]$ (0.21 g) and mqp (0.30 g) in cyclohexane was refluxed for 9 h. Solvent was removed from the filtered solution to give the crude product as a white powder. Cooling a diethyl ether extract gave white *crystals* (0.28 g, 60%).

X-Ray Crystallography of [$PdCl_2$(mqp)], (2).—The crystal system and preliminary unit-cell parameters were determined from oscillation and Weissenberg photographs. The accurate cell dimensions were obtained from least-squares refinement of the setting angles for 25 reflections ($16 < \theta < 18°$) automatically centred on a Nonius CAD4 diffractometer at the beginning of data collection. The space group ($P2_1/c$) was uniquely determined from the systematic absences, $0k0$ for k odd and $h0l$ for l odd. The density was measured by the flotation method.

Crystal data. $C_{19}H_{28}Cl_2NPPd\cdot0.8CH_2Cl_2$, $M = 546.7$, Monoclinic, $a = 12.936(3)$, $b = 13.108(3)$, $c = 15.085(3)$ Å, $\beta = 100.48(2)°$, $U = 2\,515.2$ Å^3, space group $P2_1/c$ (C^5_{2h}, no. 14), $D_m = 1.42$ g cm^{-3}, $Z = 4$, $D_c = 1.44$ g cm^{-3}, μ(Mo-K_α) = 10.9 cm^{-3}, λ(Mo-K_α) = 0.710 69 Å.

Intensities of 4 907 reflections ($\pm h, k, l$; $1.5 < \theta < 25°$) were recorded on the CAD4 diffractometer with graphite-monochromatised Mo-K_α radiation, an ω—2θ scan method, and a crystal of dimensions 0.25 × 0.10 × 0.08 mm. Periodic check of two standard reflections did not show any significant variations in their intensities during data collection. All data were corrected for Lorentz and polarisation effects but not for absorption or extinction. Averaging equivalent reflections and omitting those with $F_o < 4\sigma(F_o)$ yielded 3 490 unique reflections.

TABLE 8

Non-hydrogen atomic fractional co-ordinates (× 10^5 for Pd; × 10^4 for others) and site occupancies (× 10^2) of the disordered solvent

Atom	*x*	*y*	*z*
Pd	24 724(3)	23 131(3)	20 952(2)
Cl(1)	972(1)	2 563(1)	929(1)
Cl(2)	3 379(1)	3 556(1)	1 485(1)
P(1)	3 589(1)	2 250(1)	3 407(1)
N(1)	1 752(3)	1 136(3)	2 676(2)
C(1)	2 600(4)	1 900(4)	4 088(3)
C(2)	1 770(4)	1 240(4)	3 562(3)
C(3)	1 072(5)	735(5)	4 008(4)
C(4)	331(5)	116(6)	3 528(4)
C(5)	−336(5)	−826(6)	2 137(4)
C(6)	−212(6)	−1 105(5)	1 289(4)
C(7)	600(5)	−693(5)	921(4)
C(8)	1 274(4)	40(4)	1 336(3)
C(9)	1 122(4)	381(4)	2 198(3)
C(10)	351(5)	−104(5)	2 610(4)
C(11)	2 185(5)	342(5)	908(4)
C(12)	4 578(4)	1 201(4)	3 485(3)
C(13)	4 010(5)	175(4)	3 381(4)
C(14)	5 184(5)	1 334(5)	2 701(4)
C(15)	5 336(5)	1 187(5)	4 389(4)
C(16)	4 155(4)	3 467(4)	3 933(3)
C(17)	3 322(5)	4 303(4)	3 685(4)
C(18)	4 407(5)	3 368(5)	4 976(4)
C(19)	5 157(5)	3 761(5)	3 589(4)

Solvent molecule

	x	*y*	*z*	*K*
SL(1)	7 631(8)	2 878(8)	5 653(8)	82(2)
SL(2)	8 142(8)	3 309(11)	7 705(7)	76(2)
SL(3)	7 629(16)	2 102(17)	7 258(16)	43(2)
SL(4)	7 394(17)	2 113(17)	6 604(17)	40(2)
SL(5)	8 439(19)	2 679(22)	6 744(17)	36(2)
SL(6)	8 387(21)	3 325(27)	6 565(19)	30(2)
SL(7)	8 045(13)	2 213(12)	5 252(12)	49(2)
SL(8)	7 314(16)	2 684(17)	6 154(16)	45(2)
SL(9)	7 746(17)	2 155(17)	5 893(16)	41(2)
SL(10)	7 992(17)	2 694(24)	7 511(16)	42(2)

The palladium atom was located from a three-dimensional Patterson map and other atoms from successive electron-density syntheses. Full-matrix least-squares refinement of the non-hydrogen atoms, first with isotropic and then anisotropic temperature factors, reduced the R to 0.11 and 0.068 respectively. A difference map computed at this stage showed several peaks of significant electron density in open regions of the unit cell, which suggested the presence of disordered solvent molecules (methylene chloride) in the crystal. Ten of these peaks were assigned. Scattering factors for carbon and their positional parameters and site occupancies were refined with U_{iso} fixed at 0.08 Å^2. All the hydrogen atoms in the structure were also located from difference maps, and isotropically refined with the C–H distance constrained at 1.08 Å. The refinement converged at $R = 0.047$ and $R' = [\Sigma(w\Delta F^2)/\Sigma(wF_o^2)]^{\frac{1}{2}} = 0.059$. The weighting scheme $w = 1/[\sigma^2(F_o) + 0.000\,5F_o^2]$ gave satisfactory agreement analyses. A final difference map contained two peaks (*ca.* 1 e Å^{-3}) near the palladium atom but no other peaks of any significance.

The final non-hydrogen atomic fractional co-ordinates together with their estimated standard deviations are given in Table 8. Hydrogen-atom parameters, thermal parameters, and lists of observed and calculated structure factors are deposited in Supplementary Publication No. SUP **22814** (22 pp.).* All calculations were performed on the Queen Mary College ICL 1904S and University of London CDC-7600 computers using the programs SHELX-76 [14] for structure solution and refinement, XANADU [15] for least-squares plane calculations, and PLUTO [16] for diagrams. Neutral-atom scattering factors were taken from refs. 17 (H) and 18 (Pd,Cl,P,N,C) with those of the heavier elements being modified for anomalous dispersion ($\Delta f'$ and $\Delta f''$ values from ref. 19).

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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