Dipyrromethene Complexes of Transition Metals. Part III.† Physical Properties and Crystal and Molecular Structure of a Mixed-ligand Complex of Palladium(II)

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Complexes have been formed between bivalent palladium and the dipyrromethene ligands 4,4′-bis(ethoxycarbonyl)-3,3′,5,5′-tetramethyldipyrromethene (mpmH) and 3,4′-bis(ethoxycarbonyl)-5-chloro-3′,4,5′-trimethyldipyrromethene (cpmH) of the type $Pd_2Cl_2L_2$ (L = mpm or cpm) and PdXL(LH) (X = Cl or Br; L = mpm or cpm; LH = mpmH or cpmH). The latter complexes contain both bi- and uni-dentate co-ordinated dipyrromethene ligands. The ^1H n.m.r. and u.v.–visible spectra of these complexes have been investigated and an *X*-ray determination (diffractometer data) of the crystal and molecular structure of PdCl(cpm)(cpmH) is reported. The palladium atom is in an essentially square planar environment bonded to three nitrogen atoms and one chlorine atom. The uni- and bi-dentate dipyrromethene ligands deviate considerably from planar configurations. The unco-ordinated nitrogen atom lies above the palladium square plane but does not seem chemically bonded to any atom in the plane. Crystals are monoclinic, space group *Cc*, $Z = 4$, $a = 1782(1)$, $b = 2096(1)$, $c = 1038(6)$ pm, $\beta = 95{\cdot}47(3)°$. The structure was solved by Patterson and Fourier methods and refined by least-squares techniques to *R* 5·7% (2257 independent reflections).

METAL complexes of dipyrromethenes of general formulae ML_2 (M = Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II}, Hg^{II}, and Pd^{II}) have been discussed in two previous papers in this series.[1,2] Except for the palladium complexes, the structure of one of which is now discussed, all are known to have tetrahedral, or distorted tetrahedral, configurations about the metal ion.

Palladium(II) has been reported as forming two other types of complexes with dipyrromethenes,[3] both of which contain co-ordinated chlorine. All three types of complex are formed when dipyrromethene ligands react with the $PdCl_4^{2-}$ anion. Porter [3] formulated the chloro-complexes $Pd_2Cl_2L_2$ as chloro-bridged dimeric species, containing two bidentate dipyrromethene ligands, and compounds of stoicheiometry PdL_2HCl were formulated as monomeric containing both uni- and one bi-dentate co-ordination of the dipyrromethene ligand. Porter considered that palladium was either in three- or four-co-ordination in the latter type of compounds.

We have investigated a number of complexes of palladium, of the type described by Porter, with the dipyrromethene ligands 4,4′-bis(ethoxycarbonyl)-3,3′,-5,5′-tetramethyldipyrromethene (mpmH) and 3,4′-bis(ethoxycarbonyl)-5-chloro-3′,4,5′-trimethyldipyrromethene (cpmH).

The reaction of K_2PdCl_4 in aqueous solution with ethanolic solutions of the ligands mpmH and cpmH gave three products of general formulae PdL_2, $Pd_2Cl_2L_2$, and PdCl(L)(LH) in approximately equal proportions. All three products could be identified in admixture by their ^1H n.m.r. spectra and were separated from each other by virtue of their different solubility in water–ethanol. Reactions of the ligands with K_2PdBr_4 gave only two identifiable products: PdL_2 and PdBrL(LH). No evidence was found under these conditions for the formation of a bromo-bridged complex.

Preparations were attempted using other salts of the type K_2PdX_4 (X = I^-, SCN^-, and CN^-) and also with K_2PtCl_4 and K_2PtBr_4. No evidence was found for complex formation in any of these systems.

Crystal and Molecular Structure of PdCl(cpm)(cpmH)

Single crystals of PdCl(cpm)(cpmH) suitable for *X*-ray work were obtained, together with microcrystallites, by slow evaporation of an acetone solution of the complex, as opaque purple plates. Preliminary precession photographs indicated monoclinic symmetry. Cell dimensions were obtained by least-squares refinements of the setting angles of 12 reflections accurately centred on a computer controlled 4-circle diffractometer.

Crystal Data.—$C_{36}H_{41}Cl_3N_4O_8Pd$, $M = 869{\cdot}9$, Monoclinic, $a = 1782(1)$, $b = 2096(1)$, $c = 1038(6)$ pm, $\beta = 95{\cdot}47(3)°$,‡ $U = 3859 \times 10^6$ pm^3, $D_m = 1{\cdot}52$ (by flotation), $Z = 4$, $D_c = 1{\cdot}50$, $F(000) = 1784$, Mo-K_α radiation, $\lambda = 70{\cdot}93$ pm, μ(Mo-K_α) = 7·6 cm^{-1}. Space group *C*2/*c* or *Cc* from systematic absences: *h*0*l* for *l* odd, *hkl* for *h* + *k* odd; the former with 8 general equivalent positions, would necessarily impose two-fold symmetry in the molecule, while the latter, with 4 general positions, imposes no crystallographic symmetry and has been shown, by this analysis, to be correct.

The crystal used for data collection was mounted in a random orientation, and was an approximate rectangular prism with dimensions 0·06 × 0·11 × 0·20 mm³. For absorption correction purposes the crystal boundaries were defined by six intersecting planes.

Intensity data were collected out to a Bragg angle $\theta = 23°$ using a Hilger and Watts Y 290, computer-controlled four-circle diffractometer. The θ—2θ scan technique was used with a symmetric scan of 0·45° taken about the calculated peak position. The scan time was 1 min and stationary-counter–stationary crystal background counts of 15 s were taken at each end of the scan.

Each intensity (*I*) was corrected for background using the formula $I = CT - 2(B_1 + B_2)$. The estimated standard

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† Part II, ref. 2.

‡ Throughout this paper values in parentheses are estimated standard deviations in the least significant digits, usually derived from the inverse matrix in non-linear least-squares refinement calculations.

[1] J. E. Ferguson and C. A. Ramsay, *J. Chem. Soc.*, **1965**, 5222.

[2] Part II, F. C. March, D. A. Couch, K. Emerson, J. E. Fergusson, and W. T. Robinson, *J. Chem. Soc.* (*A*), **1971**, 440.

[3] C. R. Porter, *J. Chem. Soc.*, **1938**, 368.

deviation $[\sigma(I)]$ was given by the expression: $[\sigma(I)] = [(CT + (t_c/2t_b)^2(B_1 + B_2) + (pI)^2]^{\frac{1}{2}}$ where CT is the total integrated count, B_1 and B_2 are two background counts on either side of the peak, t_c and t_b are the times for the peak and background counts respectively and p is a factor introduced to avoid over weighting of the intense reflections.[4] Initially p was 0·075, however a value of 0·070 was gound to give the most constant values of $\Sigma(|F_o| - |F_c|)^2$ for all ranges of intensity during the final stages of refinement.

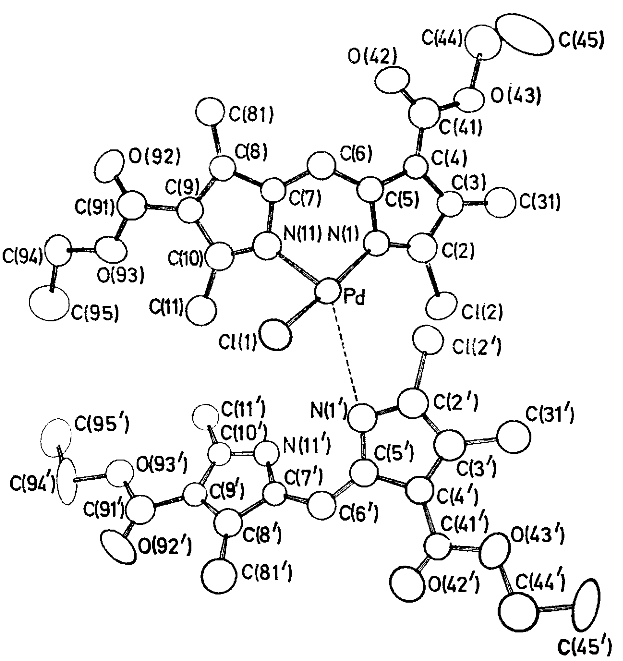

FIGURE 1 A diagram of the molecule showing the numbering of the atoms. Dotted line Pd · · · N(1′) is a bond displaced for clarification

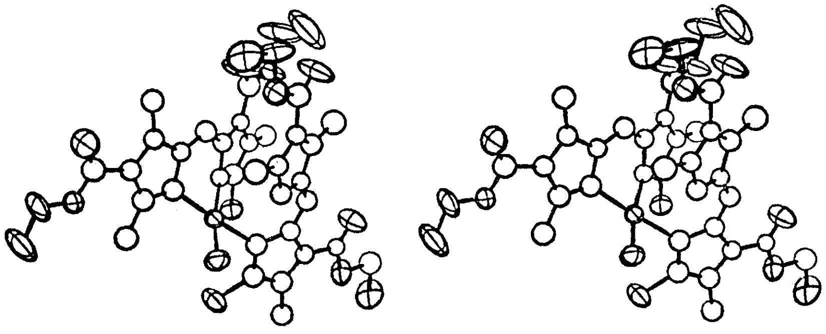

FIGURE 2 Stereo-pair

Three axial reflections, monitored as standards throughout the data collection, showed no significant variation in intensity.

The reflections $\pm hkl$ and their Friedel equivalents were collected. Preliminary investigation of the intensity statistics indicated that the space group was non-centric (therefore Cc). After averaging of equivalent reflections 2959 independent intensities were obtained (including non-equivalent Friedel pairs), of which 702 had $I < 3\sigma(I)$ and were not used in the structure refinement.

Structure Solution and Refinement.—A three-dimensional Patterson synthesis revealed the position of the palladium but not of the chlorine atoms. Least-squares refinement on F [with $\sigma(F) = 0{\cdot}5\sigma(F^2)/F$] of the Pd y co-ordinate and isotropic temperature factor, and the scale factor yielded values of R 37·1 and R' 40·5% $\{R' = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{\frac{1}{2}}\}$. In all calculations of F_c scattering factors for carbon, nitrogen, oxygen, chlorine, and palladium(0) were taken from ref. 5. Corrections for anomalous dispersion[6] for chlorine and palladium[7] were included at later stages of the refinement.

Successive difference-Fourier calculations, with intermediate least-squares refinement[8] eventually revealed all non-hydrogen atoms except for one terminal side-chain carbon atom [C(45)] (see Figure 1).

Isotropic refinement of this model, using data for which $F_o \geqslant 3\sigma(F_o)$ gave values of R 10·8 and R' 14·3%, which were reduced to 6·0 and 7·3% by anisotropic refinement of the palladium and chlorine atom temperature factors and then of all ethyl ester side-chain atoms. The latter step is felt to be justified since the isotropic temperature factors for these atoms are uniformly higher than those of the other light atoms in the structure. The last carbon atom did not show above background in a difference-Fourier computed at this stage: its co-ordinates were calculated, by comparison with the positions of the other terminal carbon atoms of the ethyl ester side chains with respect to each of the remaining atoms in these groups, and were refined successfully.

Both this and the adjacent atom [C(44)] were found to have very much higher thermal parameters than any of the other light atoms in the molecule, which may explain the difficulty experienced in its location from difference-Fourier maps. Refinement of this model gave R 5·7 and R' 6·8%, while the inverse configuration led to values of 5·6 and 6·7%. These differences are significant and we take them to indicate the correct chirality of the space group.

Figure 1 defines the atom numbering scheme used. In this diagram the unidentate ligand has been detached and drawn in the same approximate plane as the rest of the

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[4] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 197.

[5] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, Table 3.3.1A.

[6] J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, 1964, **17**, 781.

[7] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[8] Computer programs used through this analysis have been fully documented elsewhere, J. R. Norton, J. P. Collman, G. Dolcetti, and W. T. Robinson, *Inorg. Chem.*, 1972, **11**, 382.

molecule. The way in which it joins to palladium and wraps around the bidentate ligand is shown in the stereopair (Figure 2).

Fractional co-ordinates and thermal parameters of the atoms are listed in Table 1. Final values of observed and calculated structure factors are listed in Supplementary Publication No. SUP 20431 (2 pp., 1 microfiche *).

TABLE 1

(*a*) Positional and isotropic thermal parameters for PdCl(cpm)(cpmH)

Atom	*x*	*y*	*z*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	−0·0	−0·1920(1)	−0·0	0·0036(1)	0·0017(1)	0·0069(1)	−0·0001(1)	−0·0005(1)	−0·0001(1)
Cl(1)	−0·1130(3)	−0·1384(2)	0·0038(5)	0·0045(2)	0·0028(2)	0·0108(6)	0·0012(2)	0·0007(3)	−0·0005(2)
Cl(2)	0·1921(3)	−0·2039(2)	0·1602(5)	0·0042(2)	0·0028(2)	0·0114(6)	−0·0008(1)	−0·0006(3)	−0·0011(2)
Cl(2′)	0·0424(3)	−0·0546(2)	0·1559(5)	0·0073(3)	0·0022(1)	0·013(7)	−0·0003(2)	−0·0029(4)	0·0010(3)
O(42)	0·0676(9)	−0·4539(6)	−0·105(2)	0·012(1)	0·0023(4)	0·025(3)	0·0013(5)	−0·009(1)	−0·0026(9)
O(43)	0·166(1)	−0·4644(6)	0·042(2)	0·011(1)	0·0018(4)	0·023(3)	0·0015(5)	−0·010(1)	−0·0015(8)
C(44)	0·163(3)	−0·538(1)	0·023(4)	0·020(3)	0·003(1)	0·031(7)	0·004(1)	−0·013(4)	−0·003(2)
C(45)	0·175(4)	−0·564(2)	0·165(5)	0·035(6)	0·005(2)	0·04(1)	−0·006(2)	−0·002(6)	0·006(3)
O(92)	−0·1486(8)	−0·2345(6)	−0·594(1)	0·0080(7)	0·0036(4)	0·010(2)	−0·0004(5)	−0·0046(9)	−0·0001(7)
O(93)	−0·1212(7)	−0·1344(5)	−0·534(1)	0·0072(6)	0·0020(4)	0·007(1)	0·0007(4)	0·0003(8)	0·0005(6)
C(94)	−0·159(1)	−0·1092(9)	−0·650(2)	0·007(1)	0·0024(6)	0·011(3)	0·0001(6)	−0·004(1)	0·002(1)
C(95)	−0·145(2)	−0·039(1)	−0·640(2)	0·013(2)	0·0024(7)	0·020(4)	−0·0002(9)	−0·004(2)	0·003(1)
O(42′)	0·1040(8)	−0·2804(6)	0·538(1)	0·0061(6)	0·0026(4)	0·018(2)	−0·0001(4)	−0·004(1)	0·0003(7)
O(43′)	0·1364(6)	−0·1826(6)	0·611(1)	0·0049(5)	0·0038(4)	0·009(1)	−0·0018(7)	−0·0009(7)	0·0000(7)
C(45′)	0·211(1)	−0·159(1)	0·807(2)	0·008(1)	0·0059(9)	0·012(3)	−0·0032(9)	−0·003(1)	−0·003(1)
O(92′)	−0·0977(8)	−0·5018(6)	0·039(1)	0·0081(8)	0·0016(4)	0·024(3)	0·0001(4)	−0·004(1)	0·0001(8)
O(93′)	−0·1729(7)	−0·4413(6)	−0·098(1)	0·0044(5)	0·0027(4)	0·011(2)	−0·0001(4)	−0·0005(7)	0·0000(7)
C(94′)	−0·194(1)	−0·499(1)	−0·176(2)	0·008(1)	0·0038(8)	0·022(4)	−0·0012(9)	−0·001(2)	−0·007(2)
C(95′)	−0·248(1)	−0·474(1)	−0·289(2)	0·005(1)	0·0049(8)	0·016(3)	−0·0014(7)	−0·004(2)	−0·003(1)

The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

(*b*) Positional and anisotropic thermal parameters for PdCl(cpm)(cpmH)

Atom	*x*	*y*	*z*	B $(\text{nm} \times 10)^2$
N(1)	0·0854(7)	−0·2568(6)	0·005(1)	3·4(3)
N(11)	−0·0216(7)	−0·2113(6)	−0·190(1)	4·0(3)
C(2)	0·1477(9)	−0·2676(9)	0·082(2)	4·8(4)
C(3)	0·1687(9)	−0·3318(7)	0·097(2)	3·7(4)
C(4)	0·1184(8)	−0·3619(7)	0·006(2)	3·0(3)
C(5)	0·0676(8)	−0·3172(7)	−0·052(2)	3·5(3)
C(6)	0·0102(9)	−0·3260(7)	−0·155(2)	4·0(4)
C(7)	−0·0268(8)	−0·2776(7)	−0·225(2)	3·1(4)
C(8)	−0·0664(8)	−0·2817(7)	−0·351(2)	3·3(4)
C(9)	−0·0800(9)	−0·2183(7)	−0·385(2)	3·4(4)
C(10)	−0·0500(9)	−0·1775(8)	−0·284(2)	4·1(4)
C(11)	−0·0495(9)	−0·1055(8)	−0·280(2)	4·6(4)
C(31)	0·2345(9)	−0·3538(9)	0·183(2)	5·4(4)
C(41)	0·116(1)	−0·429(1)	−0·025(2)	5·1(4)
C(81)	−0·0884(9)	−0·3417(8)	−0·422(2)	4·1(4)
C(91)	−0·1201(9)	−0·1976(9)	−0·519(2)	4·4(4)
N(1′)	0·0200(7)	−0·1773(6)	0·194(1)	4·2(3)
N(11′)	−0·0962(7)	−0·2849(6)	0·118(1)	3·7(3)
C(2′)	0·0425(9)	−0·1216(9)	0·248(2)	4·7(4)
C(3′)	0·0759(9)	−0·1280(8)	0·377(2)	4·6(4)
C(4′)	0·0726(8)	−0·1911(8)	0·408(2)	3·5(3)
C(5′)	0·0340(9)	−0·2224(8)	0·294(2)	3·8(4)
C(6′)	0·1400(9)	−0·2854(8)	0·287(2)	4·0(4)
C(7′)	−0·0403(8)	−0·3150(7)	0·199(1)	2·9(3)
C(8′)	−0·0447(9)	−0·3817(8)	0·174(2)	4·1(4)
C(9′)	−0·1032(8)	−0·3880(7)	0·072(1)	3·1(3)
C(10′)	−0·1345(9)	−0·3286(7)	0·040(2)	3·4(4)
C(11′)	−0·1915(9)	−0·3067(8)	−0·057(2)	4·7(4)
C(31′)	0·1103(9)	−0·0698(9)	0·458(2)	5·0(4)
C(41′)	0·1013(9)	−0·2241(9)	0·525(2)	3·1(4)
C(81′)	0·005(1)	−0·4325(9)	0·245(2)	5·6(4)
C(91′)	−0·119(1)	−0·4517(9)	0·007(2)	4·8(4)

RESULTS

The structure consists of well separated PdCl(cpm)(cpmH) molecules which contain cpm co-ordinated as a bidentate ligand and cpmH co-ordinated as a unidentate ligand. The shortest intermolecular non-bonded interatomic distances, not involving hydrogen, are 301 [O(42) ··· C(80′)] and 331 pm [O(92′) ··· C(95′)]. The unco-ordinated nitrogen is presumably still associated with the proton as in the free ligand. Selected bond lengths and bond angles are given in Table 2. As in Pd(mpm)$_2$ the chelate ring associated with the bidentate ligand is not planar.[2] However, in contrast to the structure of Pd(mpm)$_2$ the co-ordination environment around the palladium is not strictly planar as the dihedral angle between the planes Pd,N(1),N(11) and Pd,Cl(1),N(1′) is 13·3°. The angles around the metal atom within the two planes are close to the expected 90°. The distortions of both dipyrromethene ligands are similar to those observed in Pd(mpm)$_2$ (Tables 3 and 4).

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

The unco-ordinated pyrrole ring is positioned above the palladium square plane so that the unco-ordinated nitrogen N(11′) is directly above the metal and at a distance of 294 pm, *ca.* 90 pm greater than the Pd–N bonding distance. The plane of the pyrrole ring is inclined at 50° to the plane Pd,Cl(1),N(1′). It is clear that the free pyrrole ring effectively covers one side of the palladium co-ordination plane.

TABLE 2

Interatomic distances (pm)

(*a*) Intramolecular bonding

Pd–Cl(1)	230·9(5)	C(5)–C(6)	143(2)
Pd–N(1)	204(1)	C(7)–C(6)	138(2)
Pd–N(11)	201(1)	C(5′)–C(6′)	137(2)
Pd–N(1′)	203(1)	C(7′)–C(6′)	141(2)
N(1)–C(2)	133(2)	C(2)–Cl(2)	172(2)
N(11)–C(10)	128(2)	C(2′)–Cl(2)	170(2)
N(1′)–C(2′)	134(2)		
N(11′)–C(10′)	136(2)	C(10)–C(11)	151(2)
		C(10′)–C(11′)	143(2)
N(1)–C(5)	142(2)	C(8)–C(81)	149(2)
N(11)–C(7)	144(2)	C(8′)–C(81′)	153(2)
N(1′)–C(5′)	141(2)	C(3)–C(31)	148(2)
N(11′)–C(7′)	140(2)	C(3′)–C(31′)	157(2)
C(2)–C(3)	140(2)	C(4)–C(41)	144(2)
C(10)–C(9)	142(2)	C(9)–C(91)	156(2)
C(2′)–C(3′)	142(2)	C(4′)–C(41′)	145(2)
C(10′)–C(9′)	139(2)	C(9′)–C(91′)	151(2)
C(3)–C(4)	139(2)	C(41)–O(42)	125(2)
C(9)–C(8)	139(2)	C(91)–O(92)	118(2)
C(3′)–C(4′)	136(2)	C(41′)–O(42′)	119(2)
C(9′)–C(8′)	142(2)	C(91′)–O(92′)	116(2)
C(4)–C(5)	139(2)	C(41)–O(43)	131(2)
C(8)–C(7)	142(2)	C(91)–O(93)	133(2)
C(4′)–C(5′)	146(2)	C(41′)–O(43′)	136(3)
C(8′)–C(7′)	142(2)	C(91′)–O(93′)	140(2)
O(43)–C(44)	156(3)	C(44)–C(45)	110(5)
O(93)–C(94)	143(2)	C(94)–C(95)	150(3)
O(43′)–C(44′)	153(2)	C(44′)–C(45′)	152(2)
O(93′)–C(94′)	149(2)	C(94′)–C(95′)	153(3)

(*b*) Intermolecular non-bonding

Pd · · · Cl(2)	367·1(4)	N(1′) · · · N(11′)	311(2)
Pd · · · Cl(2′)	335·4(5)		
Pd · · · C(11)	347(2)	Cl(2) · · · N(1′)	317(1)
Pd · · · N(11′)	294(1)	Cl(2) · · · C(2′)	337(2)
		Cl(2) · · · C(3′)	357(2)
Cl(1) · · · C(11)	333(2)	Cl(2) · · · C(4′)	350(2)
Cl(1) · · · C(11′)	383(2)	Cl(2) · · · C(5′)	328(2)
Cl(1) · · · Cl(2′)	352·6(7)		
Cl(1) · · · N(11′)	329(1)		

DISCUSSION

The Pd–N bond lengths are similar to those reported and the Pd–Cl bond length is typical of other reported Pd–Cl bond lengths.

The distortion of the dipyrromethene ligands is less easy to understand in this complex compared with that in Pd(mpm)$_2$, as the main reason for the distortion in the latter compound, *viz.* molecular overcrowding between the two mpm ligands, is now removed. One of the dipyrromethene ligands is unidentate and this ligand is swung away from the co-ordination plane. However, the distortions exist and must still be due to continued molecular overcrowding. Part of the reason for the distortion in the cpmH ligand may be the positioning of the hydrogen attached to N(11′). The distance of N(11′) from the palladium is 294 and from Cl(1) 329 pm, both distances being short enough to suggest either a Pd · · · H–N or Cl · · · H–N interaction or both. (The N–H · · · Cl hydrogen-bond distance is 312 pm in N_2H_5Cl and it is estimated that a Pd · · · H–N distance would be *ca.* 280—290 pm.) Hence the possibility of the palladium being pseudo-five-co-ordinate cannot be excluded in this complex. It is likely therefore that the position of the proton on N(11′) is partly responsible for the distortion in the unidentate ligand cpmH. Only by bending can the ligand cope with both the position of the hydrogen and the repulsions from the bidentate ligand.

TABLE 3

Bond angles (°)

Cl(1)–Pd–N(1)	166·9(4)
Cl(1)–Pd–N(11)	91·6(4)
Cl(1)–Pd–N(1′)	89·0
N(1)–Pd–N(11)	88·1(5)
N(1)–Pd–N(1′)	90·7
N(11)–Pd–N(1′)	176·9
Pd–N(1)–C(2)	135(1)
Pd–N(11)–C(10)	132(1)
Pd–N(1)–C(5)	117(1)
Pd–N(11)–C(7)	116(1)
Pd–N(1′)–C(2′)	124(1)
Pd–N(1′)–C(5′)	129(1)
C(2)–N(1)–C(5)	104(1)
C(10)–N(11)–C(7)	109(1)
C(2′)–N(1′)–C(5′)	104(1)
C(10′)–N(11′)–C(7′)	110(1)
Cl(2)–C(2)–N(1)	118(1)
C(11)–C(10)–N(1)	122(2)
Cl(2)–C(2)–C(3)	126(1)
C(11)–C(10)–C(9)	129(2)
Cl(2′)–C(2′)–N(1′)	120(1)
C(11′)–C(10′)–N(11′)	119(1)
Cl(2′)–C(2′)–C(3′)	126(1)
C(11′)–C(10′)–C(9′)	134(1)
C(3)–C(2)–N(1)	115(2)
C(9)–C(10)–N(11)	109(1)
C(3′)–C(2′)–N(1′)	113(2)
C(9′)–C(10′)–N(11′)	107(1)
C(31)–C(3)–C(2)	124(1)
C(91)–C(9)–C(10)	127(1)
C(31)–C(3)–C(4)	134(1)
C(91)–C(9)–C(8)	123(1)
C(31′)–C(3′)–C(2′)	123(2)
C(91′)–C(9′)–C(10′)	129(1)
C(31′)–C(3′)–C(4′)	130(2)
C(91′)–C(9′)–C(8′)	120(1)
C(4)–C(3)–C(2)	102(1)
C(8)–C(9)–C(10)	110(1)
C(4′)–C(3′)–C(2′)	107(1)
C(8′)–C(9′)–C(10′)	110(1)
C(41)–C(4)–C(3)	126(2)
C(81)–C(8)–C(9)	130(1)
C(41)–C(4)–C(5)	124(2)
C(81)–C(8)–C(7)	126(1)
C(41′)–C(4′)–C(3′)	130(2)
C(81′)–C(8′)–C(9′)	130(1)
C(41′)–C(4′)–C(5′)	124(2)
C(81′)–C(8′)–C(7′)	125(1)
C(5)–C(4)–C(3)	110(1)
C(7)–C(8)–C(9)	104(1)
C(5′)–C(4′)–C(3′)	106(1)
C(7′)–C(8′)–C(9′)	105(1)
C(6)–C(5)–C(4)	129(1)
C(6)–C(7)–C(8)	127(1)
C(6)–C(5)–N(1)	123(1)
C(6)–C(7)–N(11)	124(1)
C(6′)–C(5′)–C(4′)	125(2)
C(6′)–C(7′)–C(8′)	125(1)
C(6′)–C(5′)–N(1′)	125(1)
C(6′)–C(7′)–N(11′)	127(1)
C(4)–C(5)–N(1)	108(1)
C(8)–C(7)–N(11)	108(1)
C(4′)–C(5′)–N(1′)	109(1)
C(8′)–C(7′)–N(11′)	108(1)
C(5)–C(6)–C(7)	125(1)
C(5′)–C(6′)–C(7′)	128(2)
C(4)–C(41)–O(42)	124(2)
C(9)–C(91)–O(92)	123(2)
C(4)–C(41)–O(43)	116(2)
C(9)–C(91)–O(93)	112(1)
C(4′)–C(41′)–O(42′)	125(2)
C(9′)–C(91′)–O(92′)	129(2)
C(4′)–C(41′)–O(43′)	111(1)
C(9′)–C(91′)–O(93′)	107(2)
O(42)–C(41)–O(43)	120(2)
O(92)–C(91)–O(93)	125(2)
O(42′)–C(41′)–O(43′)	123(2)
O(92′)–C(91′)–O(93′)	123(2)
C(41)–O(43)–C(44)	119(2)
C(91)–O(93)–C(94)	117(2)
C(41′)–O(43′)–C(44′)	113(2)
C(91′)–O(93′)–C(94′)	115(2)
O(43)–C(44)–C(45)	112(4)
O(93)–C(94)–C(95)	104(2)
O(43′)–C(44′)–C(45′)	101(1)
O(93′)–C(94′)–C(95′)	104(2)

The bend in the PdClN$_3$ plane is unexpected, especially as the bend is towards the space occupied by the ligands. However, it is possible this is a result of strong repulsions between Cl(1) and Cl(2′) which are 353 pm apart (van der Waals radius of chlorine is 180 pm), and the possible existence of a Cl(1) · · · H–N(11′) hydrogen bond.

In bis-(3,3′,5,5′-tetramethyldipyrromethenato)nickel-(II)[9] and $Pd(mpm)_2$[2] it has been observed that there are two different C–N bond lengths in each pyrrole ring, which have been explained in terms of the amount of π-delocalisation possible in each bond. The same effect is observed in the present structure for the three co-ordinated pyrrole rings. For the bidentate ligand the mean C–N (type 1) is 130 and C–N (type 2) 143 pm. For the co-ordinated pyrrole ring of the unidentate ligand C–N (type 1) is 134 and C–N (type 2) 141 pm. The difference in the two types is not so pronounced for the non-co-ordinated pyrrole: C–N (type 1) 136, C–N (type 2) 140 pm. The presence of the hydrogen bonded to N(11′) restricts the π-delocalisation in the free ring which would mean that the two C–N bonds should be of similar length and close to the longer of the two values, type 1 and 2; this is what is observed.

TABLE 4

Equations of best weighted least-squares planes in the form $AX + BY + CZ - D = 0$ where X, Y, and Z are orthogonal co-ordinates in nm × 10. The distance (nm × 10) of relevant atoms from the planes are given in square brackets

Atom	A	B	C	D	χ^2 †
Plane (1):					
Pd, N(1), N(11)	0·6563	0·7229	−0·2161	−2·9086	0·0
[Pd 0, N(1) 0, N(11) 0, Cl(1) 52·2(5), N(1′) 10(1)]					
Plane (2):					
Pd, Cl(1), N(1′)	0·4761	0·8624	−0·1720	−3·4699	0·0
[Pd 0, Cl(1) 0, N(1′) 0, N(1) 46(1), N(11) 11(1)]					
Plane (3):					
N(1), N(11), C(5)—(7)	0·7810	0·0981	−0·6168	−0·6271	18·5
[N(1) 1(1), N(11) 1(1), C(5) −3(1), C(6) 4(2), C(7) −3(1), Pd 102·19(1), C(2) −29(2), C(3) −35(2), C(4) −24(1), C(8) −37(2), C(9) −56(2), C(10) −34(2)]					
Plane (4):					
N(1), C(2)—(5)	0·6704	0·1644	−0·7235	−0·1160	19·3
[N(1) 2(1), C(2) −6(2), C(3) 3(2), C(4) −1(2), C(5) −2(2), Pd 77·76(2), Cl(2) −17·4(5), N(11) −44(1), C(6) −14(2), C(7) −44(1), C(8) −97(2), C(9) −130(2), C(10) −99(2), C(31) 2(2), C(41) 1(2), O(42) 2(2), O(43) 7(2), C(44) 23, C(45) 87]					
Plane (5):					
N(11), C(7)—(10)	0·9173	0·0413	−0·3959	−0·4254	4·8
[N(11) 2(1), C(7), −2(1), C(8) 1(2), C(9) 0(2), C(10) −2(2), Pd 59·16(0), N(1), 55·7(6), C(2) −35(2), C(3) −156(2), C(4) −117(1), C(5) −66(1), C(6) −23(2), C(81) 7(2), C(11) −7(2), C(91) −3(2), O(92) 10(1), O(93) −13(1), C(94) −12, C(95) −36]					
Plane (6):					
N(1′), C(2′)—(5′)	0·9312	−0·1573	−0·3289	−0·0622	10·5
[N(1′) −2(1), C(2′) 2(2), C(3′) 0(2), C(4′) −2(1), C(5′) 3(2)' Pd −57·07(2), Cl (2′) −15·0(6), N(11′) 123(1), C(6′) 13(2), C(7′) 55(1), C(8′) 29(2), C(9′) 81(1), C(10′) 138(2), C(31′) −3(2), C(41′) −10(2), O(42′) −27(1), O(43′) −18(1), C(44′) −47(2), C(45′) −49]					
Plane (7):					
N(11′), C(7′)—(10′)	0·7225	0·1167	−0·6815	2·8420	1·4
[N(11′) 0(1), C(7′) −1(1), C(8′) 1(2), C(9′) −1(1), C(10′) 0(2), Pd −237·25(1), N(1′) −1·16(1), C(2′) −117(2), C(3′) −59(2), C(4′) −15(1), C(5′) −46(2), C(6′) −10(2), C(81′) 5(2), C(11′) −7(2), C(91′) −15(2), O(92)′ −6(1), O(93′) −30(1), C(94′) −47, C(95′) −73]					

† Probability (P) that χ^2 exceeds a if atoms are planar (2 degrees of freedom): a 5·99, P 0·05; a 9·21, P 0·01 (G. H. Stout and L. H. Jensen, '*X*-Ray Structure Determination,' Macmillan, New York, 1968, p. 422).

Interplanar angles (°)

(1)–(2)	13·3	(3)–(4)	9·6	24·9
(1)–(3)	44·2	(3)–(5)	15·3	
(1)–(4)	44·3	(4)–(5)	24·7	
(1)–(5)	44·2	(6)–(7)	28·5	
(1)–(6)	55·4			

The differences noted[2] in the C–C(ring) bond lengths in $Pd(mpm)_2$ are not observed for the bidentate cmp but are for the co-ordinated pyrrole ring of the unidentate cpmH. Whereas the reason for the difference in the C–C bond lengths in the latter pyrrole ring may be the same as given previously it is not readily apparent why this effect, if real, does not occur for the other pyrrole rings.

The ligand cpm in the complex PdCl(cpm)(cpmH) could occur in four isomeric forms, as far as the relative positions of Cl(2) and Cl(2′) are concerned. Only one isomer is found in the solid state, and from ^1H n.m.r. evidence (see later) it would appear to be the only isomer in solution. The co-ordination of the bidentate ligand allows the maximum distance to occur between Cl(1) and Cl(2). In the case of the unidentate ligand it is somewhat surprising that the pyrrole ring with the chlorine attached [at C(2′)] is the co-ordinated ring, since the nitrogen, N(1′), would have reduced σ-donor ability compared with N(11′). On the other hand, the π-acceptor ability of the ring would be enhanced by the presence of the chlorine on the pyrrole ring. This latter effect is presumably dominant.

TABLE 5

^1H N.m.r. data; δ values (p.p.m.) downfield from tetramethylsilane

Compound	Methine	Methyl attached to C(X)
$Pd_2Cl_2(mpm)_2$	7·22	2·60 (A), 2·48 (B)
$Pd_2Cl_2(cpm)_2$	8·18	2·63 (A), 2·52 (B), 2·22 (C)
PdCl(mpm)(mpmH)	6·95, 6·73	3·55 [C(2′)], 2·88 [C(10)], 2·48 [C(8), C(8′)], 2·35 [C(4),C(4′)], 2·30 [C(10′)], 1·67 [C(2)]
PdBr(mpm)(mpmH)	6·92, 6·73	3·55 [C(2′), 2·88 [C(10)], 2·48 [C(8),C(8′)], 2·42 [C(4)], 2·32 [C(4′)], 2·27 [C(10′)], 1·67 [C(2)]
PdCl(cpm)(cpmH)	8·00, 7·77	2·92 [C(10)], 2·52 [C(8′)], 2·38 [C(3),C(3′)], 2·27 [C(8)], 2·08 [C(10′)]
PdBr(cpm)(cpmH)	8·00, 7·80	2·92 [C(10)], 2·53 [C(8′)], 2·45 [C(3)], 2·38 [C(3′)], 2·27 [C(8)], 2·08 [C(10′)]

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[9] F. A. Cotton, B. G. De Boer, and J. R. Pipal, *Inorg. Chem.*, 1970, **9**, 783.

^{1}H *N.m.r. Spectra*

The ^{1}H n.m.r. spectra of several diamagnetic complexes of general formulae ML_2 have been discussed previously in this series;[2] the spectra found for the mixed-ligand complexes differ in several respects from these. Chemical shift data are summarised in Table 5 and Figure 3.

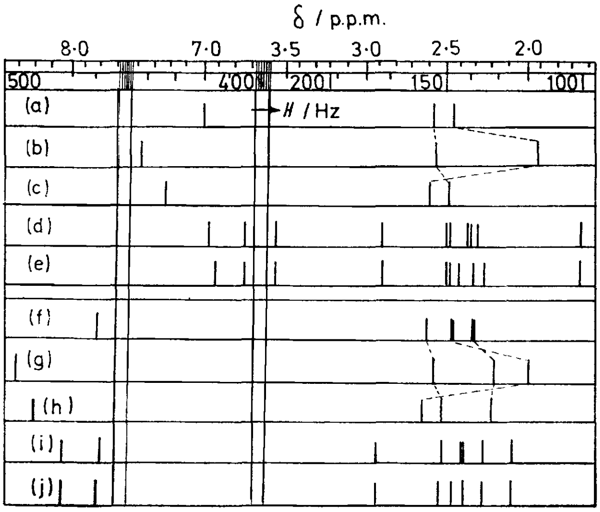

FIGURE 3 Summary of the relative chemical shifts of the methyl and methine protons: (a) mpmH, (b) $Pd(mpm)_2$, (c) $Pd_2Cl_2(mpm)_2$, (d) PdCl(mpm)(mpmH), (e) PdBr(mpm)(mpmH), (f) cpmH, (g) $Pd(cpm)_2$, (h) $Pd_2Cl_2(cpm)_2$, (i) PdCl(cpm)(cpmH), (j) PdBr(cpm)(cpmH)

Bridged Complexes $Pd_2Cl_2L_2$.—The ^{1}H n.m.r. spectra of these complexes are comparitively simple and resonance assignments can be made readily. The simplicity of the spectra indicate that the ligand co-ordination is symmetric with both pyrrole rings of the ligands equivalently co-ordinated in the dimer.

The ethyl ester side chains give rise to two sets of resonances with chemical shifts of *ca.* 1·3 and 4·3 p.p.m. These resonances are similar in all respects to those found for the side-chains of the ML_2 series.

The ring-substituted methyl groups are designated as methyl groups (A) and (B) for $Pd_2Cl_2(mpm)_2$ and (A), (B), and (C) for $Pd_2Cl_2(cpm)_2$ as described for the ML_2 compounds,[2] and resonances due to these groups can be assigned in the same way as for the ML_2 compounds. The group (A) resonance is moved down field when the ligand co-ordinates to the $PdCl_2Pd$ group, to *ca.* 2·6 p.p.m. This deshielding is explained in terms of a decrease in electron density in the region of the nitrogen atom on co-ordination. In contrast this methyl group is considerably shielded on co-ordination to Pd in PdL_2 and this difference in behaviour is explained in terms of the interaction of the methyl protons with the shielding cone of the adjacent pyrrole ring of the other ligand in the latter compounds. This interaction does not occur in the bridged complexes. The shielding of the (B) and (C) methyl groups on co-ordination may be explained in terms of decreased ring currents in the pyrrole rings corresponding to the withdrawal of electrons on co-ordination.

It is unlikely that the two possible isomers of $Pd_2Cl_2(cpm)_2$ would show up in the ^{1}H n.m.r. spectra though thin-layer chromatography suggests that both exist.

The methine proton is considerably deshielded on co-ordination of the ligand, although to a lesser extent than that found for the corresponding proton in the PdL_2 complexes.

PdX(L)(LH) *Complexes* (X = Cl *or* Br).—The spectra of the PdX(L)(LH) complexes are more complicated than those of both the bridged complexes and the ML_2 complexes. The presence of two methine proton resonances, and the complexity of the resonances due to the ring-substituted methyl groups is in accord with the presence of two dipyrromethenes which are chemically distinguishable.

The resonances due to the ethyl ester side-chains form complicated overlapping patterns centred at about the same positions as observed for the other complexes studied by ^{1}H n.m.r. This is to be expected since there are four chemically distinguishable pyrrole rings per complex.

A partial and tentative assignment of methyl proton resonances is possible by comparison of the spectra of the cpm and mpm complexes (Figure 3). The ^{1}H n.m.r. spectra of the cpm complexes indicate that, as in the solid state, only one isomer is formed. If more than one isomer was present in solution a more complex pattern of resonances could be expected.

Two widely separated methyl group resonances (at 3·55 and 1·67 p.p.m.) are observed for the mpm but not for the cpm complexes. It is reasonable to assign these resonances to the methyl groups in the former which replace the chlorine atoms in the latter [*i.e.* at carbons C(2) and C(2′) in Figure 1]. Of these, the strongly shielded group at 1·67 p.p.m. is probably the methyl substituted at C(2) since the protons of this group will be positioned above the centre of the nearest pyrrole ring of the unidentate ligand and consequently will be well within the shielding cone of this ring (see Figure 6 in ref. 2). The observed shielding of the group by 1 p.p.m. appears quite reasonable. The resonance at 3·55 p.p.m. will therefore be due to the methyl substituted at C(2′). The strong deshielding is unexpected but may be due to an interaction with the chlorine [Cl(1)] co-ordinated to the palladium [the Cl(2′) · · · Cl(1) distance is 353 pm]. The methyl groups substituted at C(10) and C(10′) in both mpmH and cpmH can be treated in the same way as the aforementioned methyl groups. The methyl group on C(10′) lies above a pyrrole ring of the other ligand and will lie within the shielding cone and it is therefore assigned to resonances 2·30 and 2·08 p.p.m. for the mpm and cpm ligands. The methyl group on C(10) is also close to the co-ordinated halogen (333 pm) and will be deshielded by this interaction and hence the methyl group C(11) is assigned to the resonances 2·88 and 1·92 p.p.m. for the mpm and cpm ligands. The difference between the magnitude of the shielding of the methyl groups on C(2) and C(10′), deshielding of methyl groups on C(2′) and C(10) and the shielding of the methyl group on C(10′) for the mpm and cpm ligands may be due to differences arising from the position of the unidentate ligand in the mpm and cpm complexes. However, this cannot be verified as the molecular structure of the complex PdCl(mpm)(mpmH) is unknown.

The remaining resonance peaks are in similar positions for all the complexes and are assigned to the remaining methyl groups, which are less affected by the mode of co-ordination and stereochemistry of the dipyrromethene ligands. Tentative assignments are given in Table 5.

Two resonances with equal integrals are observed in the methine proton region of the spectrum. The two resonances are consistent with the two modes of co-ordination of the ligands. In the mpm complexes both methine protons are shielded and in the cpm complexes one is shielded and one deshielded with respect to the methine proton of the free ligands. In view of the fact that the methine protons are strongly deshielded in all the other dipyrromethene complexes studied, the difference in behaviour of the protons in these complexes appears anomalous, especially as the configuration of the bidentate ligand in PdCl(cpm)(cpmH) has been shown to be basically the same as for mpm in the complex $Pd(mpm)_2$. It should be noted that the behaviour exhibited here is similar to that found from studies of acetylacetonate and porphyrin complexes. If the strong deshielding found for the ML_2 complexes results from increased conjugation around the six-membered chelate ring as a result of complex formation it is difficult to see why this does not occur for the bidentate ligand of the PdX(L)(LH) complexes. If this effect is important then it allows the resonance to be assigned at higher field to be that due to the methine proton on the monoco-ordinated ligand where no chelate ring is formed.

U.v.–Visible Spectra

The u.v.–visible spectra obtained for the palladium mixed-ligand complexes are very similar in many respects to those of the ML_2 complexes discussed in ref. 2; however, interesting differences are found. As before the spectra can be divided into three regions: (i) one or two very intense bands (ε *ca.* 10^5), in the region of 20,000 cm^{-1}, are assigned to a low energy $\pi \rightarrow \pi^*$ intraligand transition; (ii) a band near 26,000 cm^{-1} (ε *ca.* 10^3) is assigned to a metal–ligand charge-transfer transition; and (iii) high-energy $\pi \rightarrow \pi^*$ intraligand transitions are observed above 30,000 cm^{-1}. No ligand-field bands are observed for these complexes, presumably because the lowest energy ligand-field band is masked by the low energy $\pi \rightarrow \pi^*$ transition (Table 6).

Bridged Complex, $Pd_2Cl_2(MCLPM)_2$.—As with most of the monomeric ML_2 complexes for the low energy $\pi \rightarrow \pi^*$ transition for the bridged complex has one dominant band with a shoulder to higher energy. The intensity of the band is approximately the same as for the neutral ligand and is at lower energy than for $Pd(MClPM)_2$. The charge-transfer band is of about the same intensity and is in about the same position as for $Pd(MClPM)_2$. The high energy $\pi \rightarrow \pi^*$ bands are poorly resolved.

TABLE 6

U.v.–visible spectra: ν (cm^{-1}) with molar extinction coefficients ($\varepsilon \times 10^{-4}$) in parentheses

Compound	Low-energy $\pi \rightarrow \pi^*$ band	Charge-transfer band	High-energy $\pi \rightarrow \pi^*$ band
$Pd_2Cl_2(cpm)_2$	18,350 (5·6), 18,900sh	25,900 (1·1)	31,400sh
PdBr(mpm)(mpmH)	21,008 (7·1), 19,800sh	25,640 (0·8)	34,500sh
PdCl(cpm)(cpmH)	19,700 (5·2), 18,400sh	25,600sh	31,600sh, 37,400sh
PdBr(cpm)(cpmH)	18,380 (4·2), 19,880 (4·7)	25,100sh	31,300sh, 35,800sh

PdX(L)(LH) *Complexes*.—Two bands are found in the low energy $\pi \rightarrow \pi^*$ region. The band at lowest energy is usually poorly resolved and is observed as a prominent shoulder on the side of the main band. The composite spectrum is presumed to be due to the presence of the two dipyrromethene ligands which have different modes of co-ordination. The band at higher energy may be due to the unidentate, and that at lower energy to the bidentate ligand, since the relative positions of the two bands are similar to those of the protonated ligands and the bridged complexes respectively. The band intensities are comparable with the intensities of those for the free ligands.

For each complex a band which is assigned to a metal–ligand charge-transfer is observed at *ca.* 25,000 cm^{-1}.

Preparation of Complexes and Physical Measurements.—The ligands mpmH and cpmH were prepared by the methods of refs. 10 and 11.

Palladium complexes. The complexes PdX(L)(LH) were prepared by slowly adding the ligand, dissolved in the minimum of ethanol, with a little sodium acetate to a concentrated solution of K_2PdCl_4 (or K_2PdBr_4). After several hours microcrystalline precipitates appeared which were recrystallised from chloroform and then acetone [except for PdCl(mpm)(mpmH) which decomposed during attempted recrystallisation]. Analytical data are summarised in Table 7.

The complexes $Pd_2Cl_2L_2$ were obtained from the appropriate mother liquors by evaporation under a stream of air and were recrystallised from acetone or chloroform. Analytical data are summarised in Table 7. These are not good but the complexes are clearly characterised by their ^1H n.m.r. spectra.

Physical measurements. U.v.–visible spectra were obtained for chloroform solutions by use of either a Beckman

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[10] D. P. Mellor and W. H. Lockwood, *Proc. Roy. Soc. New South Wales*, 1940, **74**, 141.

[11] H. Fischer, E. Sturm, and H. Friedrich, *Annalen*, 1928, **461**, 267.

TABLE 7

Analytical data for the metal complexes

	Found (%)				Required (%)		
	C	H	N	Formula	C	H	N
$Pd_2Cl_2(mpm)_2$	40·1	4·5		$C_{38}H_{46}Cl_2N_4O_8Pd_2$	47·0	4·75	
$Pd_2Cl_2(cpm)_2$	44·7	4·4	5·5	$C_{36}H_{40}Cl_4N_4O_8Pd_2$	42·7	4·0	5·5
PdCl(mpm)(mpmH)	56·4	4·0	4·4	$C_{38}H_{47}ClN_4O_8Pd$	55·0	5·6	6·8
PdBr(mpm)(mpmH)	51·7	5·4	6·3	$C_{38}H_{47}BrN_4O_8Pd$	52·2	5·3	6·4
PdCl(cpm)(cpmH)	50·5	4·9	6·3	$C_{36}H_{41}Cl_3N_4O_8Pd$	49·7	4·4	6·4
PdBr(cpm)(cpmH)	47·3	4·6	6·3	$C_{36}H_{41}BrCl_2N_4O_8Pd$	47·2	4·2	6·1

DK 2A or a Shimadzu Multipurpose Spectrophotometer; ^1H n.m.r. spectra were obtained for deuteriochloroform solutions by use of a Varian A 60 spectrometer, with tetramethylsilane and chloroform as internal standards.

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