Pentamethylcyclopentadienyl-rhodium and -iridium Complexes. Part 26.[1] Dicationic η^5-Aniline and η^6-Anisole Complexes

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The preparation and properties of a series of dicationic aniline and substituted aniline complexes $[M(C_5Me_5)(p\text{-}R^1C_6H_4NR^2R^3)][PF_6]_2$ (M = Rh or Ir; $R^1 = R^2 = R^3 = H$; $R^1 = R^2 = H$, R^3 = Me or Ph; $R^1 = H$, $R^2 = R^3 = Me$; $R^1 = R^2 = R^3 = Me$; $R^1 = Me$, $R^2 = R^3 = H$) are described. From the ^1H and ^{13}C n.m.r. spectra and the i.r. spectra it is concluded that a 6-imino-1—5-η-cyclohexadienyl form is a significant contributor to the bonding in these complexes and accounts, for example, for the barrier to rotation about the C–N bonds observed in the *N*-methylaniline and diphenylamine complexes. This was confirmed by the single-crystal *X*-ray structure of $[Rh(C_5Me_5)(PhNHMe)][PF_6]_2$ even though disorder and rather large estimated standard deviations preclude very accurate bond-length and bond-angle measurements. The related anisole complexes $[M(C_5Me_5)(PhOMe)][PF_6]_2$ were also prepared. Their n.m.r. spectra are not characteristic of an η^5-bonded benzene ring, and it is proposed that the anisole is η^6-bonded. The rhodium–anisole complex is labile and the anisole is easily displaced by acetone; it is concluded that OMe does *not* significantly stabilise η^6-arene binding in these complexes in contrast to methyl which does.

IN previous papers of this series we have described cationic rhodium and iridium sandwich complexes of the type $[M(C_5Me_5)(arene)]^{2+}$ where arene = benzene and methylbenzenes,[2,3] polycyclic aromatics such as indene, indole, naphthalene, or phenanthrene,[3] phenol,[4] and *m*- and *p*-dihydroxybenzenes.[1] These reactions have also been reviewed briefly.[5] We now describe the preparation and properties of some complexes of this type with aniline, substituted anilines, and anisole.

RESULTS AND DISCUSSION

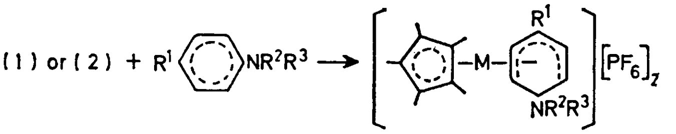
Aniline and Substituted Aniline Complexes.—The aniline and substituted aniline complexes (3)—(8) were made as shown. It was found most convenient to use the isolated tris-acetonitrile complex (1)[3] as starting material for the synthesis of the rhodium complexes; the tris(acetonitrile)iridium complex was too inert to make the corresponding iridium complexes which were obtained from the tris-acetone complex (2), prepared *in situ*.[3] In each case one equivalent of the aniline per metal gave optimum yields (Table 1); excess of amine gave red decomposition products. Analytical data (Table 1) were in good agreement with the proposed structures.

The structures of the complexes were elucidated from their n.m.r. spectra, in particular the ^{13}C n.m.r. spectra of the rhodium complexes (3a)—(8a) (Table 1 and Figure 1). Three points were immediately evident. (*i*) The aromatic resonances in all the complexes were at substantially lower frequencies (higher field) than in the free ligands. (*ii*) In the *N*-methylaniline complexes at ambient, and in the diphenylamine complexes at low temperatures, there was no plane of symmetry in the π-benzene resonances and C(1) and C(5), and C(2) and C(4) were different. (*iii*) In the rhodium complexes five of the six benzenoid resonances showed coupling to rhodium but this could not be detected in C(6), the carbon bearing the nitrogen. Furthermore, *J*(Rh–C) for C(3) was often larger than for C(1), C(2), C(4), and C(5), as for example in the aniline, *p*-toluidine, and *NN*-dimethyl-*p*-toluidine complexes (3a), (6a), and (7a) where *J*(Rh–C) = 6.1 to C(3) and 4.6 Hz to the others.

Similar, though less complete, information came from the ^1H n.m.r. spectra which showed a downfield shift of the aromatic hydrogens on complexation, the presence of a plane of symmetry in the aniline, the *p*-toluidine, the *NN*-dimethyl-aniline and -*p*-toluidine complexes [(3), (5), (6), and(7)] and the absence of such a plane in the *N*-methylaniline and (at low temperatures) the diphenylamine complexes.

$$[M_2(C_5Me_5)_2Cl_4] + 4Ag[PF_6] + \text{solvent} \longrightarrow 2[M(C_5Me_5)(\text{solvent})_3][PF_6]_2$$

(1) M = Rh, solvent = MeCN
(2) M = Ir, solvent = Me_2CO



(3a) M = Rh, R^1 = H, $R^2 = R^3$ = H
(3b) Ir, R^1 = H, $R^2 = R^3$ = H
(4a) Rh, R^1 = H, R^2 = H, R^3 = Me
(4b) Ir, R^1 = H, R^2 = H, R^3 = Me
(5a) Rh, R^1 = H, $R^2 = R^3$ = Me
(5b) Ir, R^1 = H, $R^2 = R^3$ = Me
(6a) Rh, R^1 = Me, $R^2 = R^3$ = H
(6b) Ir, R^1 = Me, $R^2 = R^3$ = H
(7a) Rh, $R^1 = R^2 = R^3$ = Me
(7b) Ir, $R^1 = R^2 = R^3$ = Me
(8a) Rh, $R^1 = R^2$ = H, R^3 = Ph
(8b) Ir, $R^1 = R^2$ = H, R^3 = Ph

TABLE 1

Analytical and ^{13}C and ^{1}H n.m.r. spectral data [a]

		Analysis (%) [b]			^{13}C N.m.r. [c]								^{1}H N.m.r. [d,e]						
	Yield (%)	C	H	N	C_5Me_5	C_5Me_5	C(1)/ C(5)	C(2)/ C(4)	C(3)	C(6)	N*Me*	C(3)*Me*	C_5Me_5	H(1)/ H(5)	H(2)/ H(4)	H(3)	NH	NMe	CMe
(3a) $[Rh(C_5Me_5)(PhNH_2)][PF_6]_2$	82	31.2 (30.9)	3.6 (3.6)	2.1 (2.3)	10.0	110.4 (7.6)	88.2 (4.6)	105.9 (4.6)	96.1 (6.1)	141.5			2.26	6.74(d) [7.3]	7.19(dd) [5.5, 7.3]	7.05(t) [5.5]	7.55(bd)		
(3b) $[Ir(C_5Me_5)(PhNH_2)][PF_6]_2$	52	26.7 (27.1)	3.3 (3.1)	1.9 (2.0)	9.6	103.7	77.5	96.4	90.0	141.5			2.37	6.87(m)	7.18(m)	7.18(m)	7.47(bd)		
(4a) $[Rh(C_5Me_5)(PhNHMe)][PF_6]_2$	90	32.2 (32.2)	3.7 (3.8)	2.1 (2.2)	10.4	110.5 (7.6)	83.1 (4.6), 87.4 (6.1)	105.2 (6.1), 105.5 (4.6)	95.5 (4.6)	143.1	30.3		2.30	6.67(d) [6.8], 6.83(d) [6.8]	7.10(t) [6.4], 7.19(t) [6.8]	6.98(t) [6.4]	8.0(bd)	3.24(d) $J(Me\text{-}NH)$ =5.1	
(4b) $[Ir(C_5Me_5)(PhNHMe)][PF_6]_2$	75	28.3 (28.2)	3.6 (3.3)	2.0 (1.9)	10.0	103.9	72.0, 75.9	95.6, 96.2	89.6	143.6	31		2.36	6.77(dd) [3.6], 6.90(dt) [2.6]	7.1(m)	7.1(m)	8.02(vbd)	3.26(d) $J(Me\text{-}NH)$ =5.1	
(5a) $[Rh(C_5Me_5)(PhNMe_2)][PF_6]_2$	92	32.7 (33.3)	3.9 (4.0)	2.2 (2.2)	10.8	110.6 (7.7)	83.0 (4.6)	104.9 (4.6)	95.3 (4.6)	n.o.	40.8		2.36	6.91(d) [7.6]	7.15(dd) [6.0, 7.6]	7.00(t) [6.0]		3.49(s)	
(5b) $[Ir(C_5Me_5)(PhNMe_2)][PF_6]_2$	76	29.1 (29.3)	3.3 (3.6)	1.9 (1.9)	10.4	104.0	71.1	95.4	89.6	145.4(?)	40.3		2.43	6.93(d) [6.8]	7.08(dd) [5.4, 6.8]	7.14(t) [5.4]		3.53(s)	
(6a) $[Rh(C_5Me_5)\{(tol)NH_2\}][PF_6]_2$	88	33.0 (32.2)	3.9 (3.8)	2.1 (2.2)	9.6	109.8 (7.6)	87.7 (6.1)	105.6 (4.6)	110.7 (6.1)	140.4		17.5	2.23	6.67(d) [7.6]	7.05(d) [7.6]		7.47(bd)		2.51(s)
(6b) $[Ir(C_5Me_5)\{(tol)NH_2\}][PF_6]_2$	28	29.5 (28.2)	3.4 (3.3)	1.9 (1.9)	9.2	103.3	77.0	96.3	105.3	140.6		17.2	2.33	6.79(d) [7.4]	7.08(d) [7.4]		7.42(bd)		2.56(s)
(7a) $[Rh(C_5Me_5)\{(tol)NMe_2\}][PF_6]_2$	84	34.1 (34.4)	4.9 (4.3)	2.1 (2.1)	10.3	110.0 (7.7)	82.3 (4.5)	104.5 (4.6)	109.6 (6)	143.4	40.8	16.8	2.39	6.79(d) [7.6]	6.94(d) [7.6]			3.46(s)	2.59(s)
(7b) $[Ir(C_5Me_5)\{(tol)NMe_2\}][PF_6]_2$	82	30.5 (30.3)	3.5 (3.8)	1.8 (1.9)	10.0	103.5	70.6	95.3	104.7	144.9	40.3	16.6	2.38	6.85(dd) [7.2]				3.52(s)	2.57(s)
(8a) $[Rh(C_5Me_5)(PhNHPh)][PF_6]_2$ [f]	83	37.3 (37.9)	3.8 (3.8)	2.0 (2.0)	10.3	110.3 (7.6)	86.4 (*ca.* 1), 87.1 (*ca.* 1)	105.0 (*ca.* 1), 105.5 (*ca.* 1)	96.5 (4.6)	139.4			2.25	7.4—7.7(m)			9.9		9.9(s)
(8b) $[Ir(C_5Me_5)(PhNHPh)][PF_6]_2$ [g]	82	33.5 (33.6)	3.1 (3.3)	1.7 (1.8)	9.9	103.6	75.4, 76.1	95.4, 96.1	90.2	139.3			2.41	7.6(m)		7.45(t) [7.0]	n.o.		
(9a) $[Rh(C_5Me_5)(PhOMe)][PF_6]_2$ [h]	82	31.4 (32.1)	3.0 (3.6)		10.2	112.1 (7.7)	93.0	107.0	101.1	147.6			2.36		7.3, 7.5(m)				
(9b) $[Ir(C_5Me_5)(PhOMe)][PF_6]_2$ [i]	60	28.2 (28.0)	1.9 (3.2)		10.1	106.2	84.9	98.0	94.5	145.1			2.53	7.63(d) [6.7]	7.53(t) [6.7]	7.39(t) [6.7]			

[a] δ Measured in $(CD_3)_2CO$; n.o. = not observed. [b] Calculated values are given in parentheses. [c] J(Rh–C) in Hz are given in parentheses. [d] ^{1}H N.m.r. spectra recorded at 220 MHz; d = doublet, t = triplet, s = singlet, m = multiplet, b = broad, vb = very broad. [e] Aromatic J(H–H) in Hz are given in square brackets. [f] ^{13}C Spectrum (at −90 °C) also shows resonances due to unco-ordinated phenyl: δ 124.6 (*o*-); 131.2 (*m*-); 128.4 (*p*-); 136.1 (*i*-). ^{1}H Resonances of unco-ordinated phenyl at δ 7.0, 7.2 (m). [g] ^{13}C Spectrum (at −90 °C) also shows resonances due to unco-ordinated phenyl: δ 124.7 (*o*-); 131.1 (*m*-); 128.7 (*p*-); 135.5 (*i*-). ^{1}H Resonances of unco-ordinated phenyl at δ 7.15, 7.23(m). [h] ^{13}C Spectrum (at −90 °C) also shows O*Me* at 59.7 and unco-ordinated PhOMe at 55.0 (O*Me*); 114.2(*o*-); 121.0 (*p*-); 130.3 (*m*-); and 159.7 (*i*-). ^{1}H shows co-ordinated O*Me* (4.29) and unco-ordinated PhOMe at 3.79 (s) and 6.95 (m). [i] O*Me* Resonances at δ 60.1 (^{13}C) and δ 4.34 (^{1}H).

These data show that the benzene ring is π-complexed to the metal and suggest (*a*), that the metal is asymmetrically bonded to the ring, being closer to C(3) than to C(6), and (*b*), that the barrier to rotation about the C(6)-N bond is significantly higher than in the uncomplexed aniline.[6]

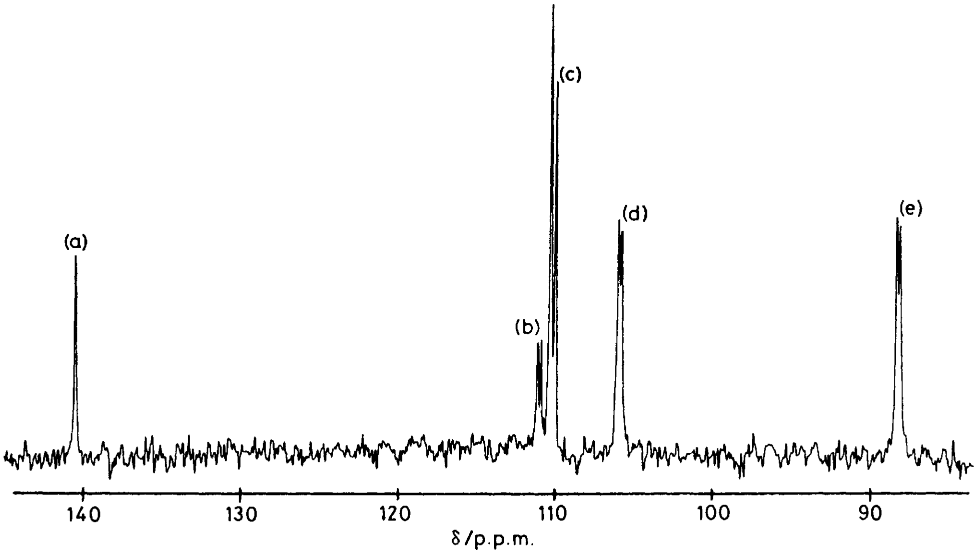
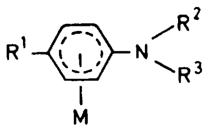


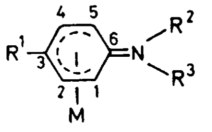
FIGURE 1 Partial ^{13}C n.m.r. spectrum of $[Rh(C_5Me_5)\{(tol)NH_2\}][PF_6]_2$ in $(CD_3)_2CO$: (a) C(6), (b) C(3), (c) C_5Me_5, (d) C(2) + C(4), and (e) C(1) + C(5)

Further evidence for a change in the nature of the aniline on co-ordination comes from the i.r. spectra. In the free anilines the strong band normally associated with ν(C-N) occurs at 1 272 ($PhNH_2$), 1 267 [$(tol)NH_2$; tol = *p*-MeC_6H_4], 1 316 (PhNHMe), 1 306 (Ph_2NH), 1 341 ($PhNMe_2$), and 1 339 cm^{-1} [$(tol)NMe_2$]. In the complexes (3)—(8) this region is devoid of such bands, but new strong bands appear at, for example, 1 572 (3a, 3b), 1 582 (4a), 1 589 (4b), 1 609 (5a), 1 620 (5b), and 1 577 cm^{-1} (6a, 6b), which we ascribe to ν(C=N), probably coupled to the ring C=C vibrations.

We conclude from all these data that a distortion of the aniline has occurred on co-ordination towards an η^5-co-ordinated iminocyclohexadienyl form (II) in place of the more normal co-ordination pattern exemplified by (I).



(I)



(II)

A similar conclusion has been drawn by Pauson and Segal[7] concerning the nature of co-ordinated anilines from the ^{1}H n.m.r. and the i.r. spectra of aniline(tricarbonyl)manganese cations.

X-*Ray Structure of* $[Rh(C_5Me_5)(PhNMeH)][PF_6]_2$.—In order to examine the change that occurs on co-ordination, the single-crystal *X*-ray structure of the *N*-methylaniline–rhodium complex (4a) was determined.

This showed the presence of two independent [Rh-$(C_5Me_5)(PhNHMe)]^{2+}$ dications in the unit cell [(A) and (B)]. In both cases, however, the *N*-methylaniline ligand was disordered so that the dications showed an apparent exact plane of symmetry through the rhodium, the PhNHMe, and the C_5Me_5 ligands. The disorder caused C(6), the aniline carbon bearing the NHMe, and the adjacent atom C(1), to become apparently coincident, and also to make C(2) and C(5), and C(3) and C(4) apparently equivalent. To show this, the numbering scheme in Figure 2 has been adopted.

The crystal structure (Table 2) shows that the C_5Me_5 rings are equivalently and symmetrically bonded to the Rh atoms [the mean Rh-C bond lengths, 2.177 for molecule (A) and 2.171 Å for (B), being normal[8]] and that the Rh atoms are significantly further (5σ, 4σ) from C(1,6) than from C(2,5) or C(3,4). The latter point confirms the conclusion reached from the values of *J*(Rh-C) found in the ^{13}C n.m.r. spectra.

Because of the disorder and the rather large estimated standard deviations (e.s.d.s) of molecules (A) and (B), the data allow few more definitive conclusions to be reached. However, as it appears from the n.m.r. data that there is a distortion towards an 1—5-η-6-iminocyclohexadienyl structure for the co-ordinated PhNHMe and since this is borne out by the asymmetric binding of the Rh to the C_6 ring shown in the crystal structure, we may reasonably assume that the positions found for C(1,6) represent an average of the true positions of C(1) and C(6).

Crystal structures of a number of 1—5-η-cyclohexadienyl metal complexes have been reported[9-13] and these all show the common features that (*i*) the metal is further from C(6) than from C(3), (*ii*) C(1), C(2), C(3), C(4), and C(5) are accurately coplanar [maximum deviation from the best plane is usually 0.01 Å, but C(3) is sometimes also bent back a little], and (*iii*) C(6) is out of the plane of the other benzenoid carbons away from the metal and the dihedral angle between the planes C(1)-C(6)-C(5) and

C(1)–C(2)–C(3)–C(4)–C(5) is usually 40—45°. The bond lengths C(6)–C(1) and C(6)–C(5) are also usually significantly longer than the other ring C–C bonds and imply that C(6) is largely sp^3 in character and that there is no bonding of the metal to it.

If we now assume that a related bonding situation occurs in complex (5a) then we can calculate a position for C(1), assuming it and C(2)–C(4)–C(5) to be coplanar. As we know the average position for C(1,6) we can also calculate a position for C(6). Based on this assumption, therefore, we have estimated that the Rh–C(1) distances are 2.265 Å [molecule (A)] and 2.289 Å [molecule (B)] and that the Rh–C(6) distances are 2.453 and 2.376 Å respectively. This gives dihedral angles of 12.5° for (A) and 13.5° for (B) between the planes C(1)–C(6)–C(5) and C(1)–C(2)–C(3)–C(4)–C(5) in the two molecules.*

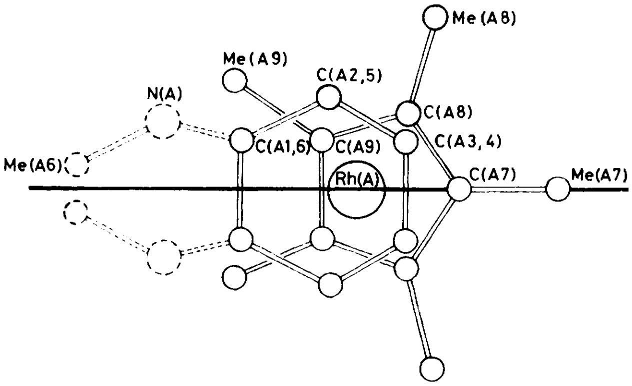


FIGURE 2 View of the cation of $[Rh(C_5Me_5)(PhNHMe)][PF_6]_2$ projected onto the C_5Me_5 plane and showing the disorder involving the PhNMe ligand; hydrogen atoms not included

Unfortunately the high e.s.d.s of the determination and the disorder present in the molecules, which affect primarily the NHMe substituent, make impossible any further definitive statements about the bonding of this group to the benzene ring, but we note that the found distances N–C(1,6) in the two molecules are quite short [1.28(4) and 1.35(4) Å respectively] and consistent with the presence of at least some C=N character in the bonding.

We conclude therefore that the *X*-ray, n.m.r., and i.r. data are all in agreement in suggesting a distortion from an η^6-benzenoid (I) towards a 6-imino-1—5-η-cyclohexadienyl binding (II) of the ring to the metal. Since the dihedral angles found in the true η^5-cyclohexadienyl complexes between the planes C(1)–C(6)–C(5) and C(1)–C(2)–C(4)–C(5) are 40—45° whereas in the complex discussed here it is about 13° we may speculate that the form (II) contributes *ca.* 30% to the overall bonding.

Although numerous π-aniline complexes have been reported [14] only one other crystal structure, of *o*-toluidine(tricarbonyl)chromium, has been determined.[15] In this structure no significant deviation of C–NH_2 from the plane of C(1)–C(5) was mentioned and the C–N bond length (1.41 Å) was normal for anilines; however, the metal was again displaced away from C(6) towards the other end of the ring [Cr–C(6) 2.37(1) Å, Cr–other ring carbons 2.20—2.26(1) Å]. This suggests that the 6-imino-1—5-η-cyclohexadienyl form (II) contributes to the structure of this molecule as well.

TABLE 2

Selected bond lengths (Å) and angles (°) in $[Rh(C_5Me_5)(PhNHMe)]^{2+}$ with e.s.d.s in parentheses

	Molecule (A)	Molecule (B)
Rh–C(1,6)	2.359(20)	2.332(19)
Rh–C(2,5)	2.250(19)	2.257(19)
Rh–C(3,4)	2.251(17)	2.254(17)
Rh–C(7)	2.167(19)	2.172(21)
Rh–C(8)	2.166(18)	2.175(19)
Rh–C(9)	2.192(16)	2.166(16)
C(1,6)–C(1,6)′	1.389(28)	1.454(27)
C(1,6)–C(2,5)	1.468(27)	1.402(27)
C(2,5)–C(3,4)	1.415(25)	1.442(26)
C(3,4)–C(3,4)′	1.391(24)	1.401(24)
C(7)–C(8)	1.425(27)	1.462(28)
C(8)–C(9)	1.455(24)	1.472(25)
C(9)–C(9)′	1.461(23)	1.392(22)
C(7)–Me(7)	1.504(32)	1.478(31)
C(8)–Me(8)	1.510(30)	1.530(29)
C(9)–Me(9)	1.542(26)	1.496(26)
C(1,6)–N	1.277(36)	1.354(36)
N–Me(6)	1.473(43)	1.468(49)
C(2,5)–C(1,6)–C(1,6)′	118.8(1.6)	119.5(1.5)
C(2,5)–C(1,6)–N	137.7(1.9)	140.2(1.8)
C(1,6)′–C(1,6)–N	103.4(1.6)	100.2(1.4)
C(1,6)–N–Me(6)	138.5(2.8)	137.4(2.8)
C(1,6)–C(2,5)–C(3,4)	121.2(1.5)	120.5(1.6)
C(2,5)–C(3,4)–C(3,4)′	120.0(1.4)	119.9(1.6)

We also note that in the i.r. spectra of $[Co\{\eta^4\text{-}C_4(tol)_4\}(PhNH_2)][BF_4]$ [16] there is no ν(CN) band at 1 272 cm^{-1} but a strong band, associated with ν(CN), is at the higher frequency of 1 564 cm^{-1}, again suggesting that a significant distortion to an iminocyclohexadienyl ligand has occurred. We therefore suggest that such distortion may well be characteristic of all π-aniline and related complexes.

Two additional points may be mentioned. First, it is noteworthy that whereas the π-*N*-methylaniline complexes (4a) and (4b) are quite static at ambient temperature, the π-diphenylamine complexes (8a) and (8b) are highly fluxional. The ^{13}C spectrum of (8a) at —90 °C shows differentiation between C(1) and C(5), and C(2) and C(4), but the couplings on these carbons are small (*ca.* 1 Hz) and hardly resolved. This suggests that even this low temperature is close to the coalescence temperature. We have not investigated this process further but we note that as the $\Delta G^‡$ for diphenylamine coalescence in (8) is clearly much less than for the *N*-methylaniline in complexes (4a) and (4b), the isomerisation may arise by move-

* Equations of the planes are of the form $lX + mY + nZ = d$ where X, Y, and Z are co-ordinates in Å referred to the axes *a*, *b*, *c*

Plane	*l*	*m*	*n*	*d*
1 C(A1)C(A2,5) C(A5,2)C(A3,4) C(A4,3)	−0.9681	0.2505	0.0000	2.227
2 C(A1)C(A6) C(A5,2)	−0.9921	0.0628	0.1086	−0.267
3 C(B1)C(B2,5) C(B5,2)C(B3,4) C(B4,3)	−0.9843	−0.1767	0.0000	−1.583
4 C(B1)C(B6) C(B5,2)	−0.9927	0.1174	−0.1174	−1.457

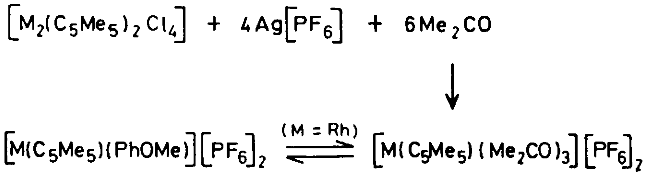
ment of a H^+ since the acidity of the NH in diphenylamine would be expected to be higher than in *N*-methylaniline. Pauson and Segal[7] were able to isolate the deprotonated diphenylamine complex $[Mn(RNC_6H_5)(CO)_3]$ by reacting $[Mn(RNHC_6H_5)(CO)_3]^+$ with base; although our complexes readily reacted with base to give deep red materials, we were unable to isolate any single substance from these reactions.

Second, the η^5-iminocyclohexadienyl formulation (II) suggests that a significant positive charge should be built up on the nitrogen. This is not, however, at all obvious in the ^{13}C chemical shifts of either the N*Me* carbons in (4), (5), and (7) or the carbons of the unco-ordinated phenyls in (8a) or (8b). All these resonances are very close to their values in the free ligands. Furthermore, the chemical shift of C(6) in all the complexes comes between δ 139 and 144 and is only slightly shifted (*ca.* 5 p.p.m.) to lower frequency from its position in the free amine. This may be due to either little change having occurred in the character of these carbons upon complexing the ligand or because there has been a balancing out of a high-frequency shift due to one cause (*e.g.* the charge) by a low-frequency shift due to another (*e.g.* complexation). We prefer the second alternative because the *X*-ray data suggest that quite significant changes in geometry have occurred on co-ordination.

π-Anisole Complexes.—The rhodium- and iridium-anisole complexes (9a) and (9b) were also made by a similar route from the tris-acetone complexes, prepared *in situ*.

To our surprise, since we had anticipated that a methoxy-substituent on the arene would stabilise the complex, either in the way that methylation has previously been shown to stabilise arene complexes or by inducing the type of η^5-bonding that we observed for the aniline complexes, we found that the rhodium complex (9a) was very labile.

In acetone solution an equilibrium is established between (9a) and free anisole and (presumably) the tris-acetone complex in which only *ca.* 50% (at 30 °C) of the anisole complex is present, as shown by the ^1H and the ^{13}C n.m.r. spectra. This implies that anisole is about as labile as benzene, which is also readily displaced from rhodium by acetone in these complexes.



$$[M_2(C_5Me_5)_2Cl_4] + 4Ag[PF_6] + 6Me_2CO \longrightarrow [M(C_5Me_5)(Me_2CO)_3][PF_6]_2 \overset{(M = Rh)}{\rightleftharpoons} [M(C_5Me_5)(PhOMe)][PF_6]_2$$

(9a) M = Rh
(9b) M = Ir

Even at −90 °C in the ^{13}C spectrum no coupling of the co-ordinated anisole carbons to rhodium could be detected. This is presumably because even this temperature is rather above the coalescence temperature for the exchange. The iridium complex (9b) is more stable, as expected from the greater inertness of the η^6-benzene complex, and does not spontaneously dissociate in acetone solution.

The ^{13}C spectra also show that $\Delta\delta$, the differences in chemical shift of the aromatic carbons * on complexing, average *ca.* 20 and 28 p.p.m. for the *o*-, *m*-, and *p*-carbons of the complexes (9a) and (9b) respectively. This is identical to $\Delta\delta$ for benzene and toluene on complexing to rhodium and iridium in such complexes[3] and is substantially less than $\Delta\delta$ for C(1)–C(5) for the anilines in complexes (3)—(8) which consistently average 23—25 (Rh) and 32—35 (Ir) p.p.m. Furthermore, $\Delta\delta$ for the anisole *i*-carbon [C(6)] is 11.3 p.p.m. for (9a) and 13.8 for (9b), about twice as great as for C(6) in the aniline complexes.

We conclude that, again on these qualitative chemical-shift arguments, the bonding in the anisole complexes more closely resembles the benzene than the aniline complexes, and that little distortion from η^6 bonding occurs there. Some support for this view comes from the *X*-ray crystal structure of anisole(tricarbonyl)chromium (as its trinitrobenzene charge-transfer complex) which shows that, within experimental error, the metal is equidistant from the six carbon atoms (Cr–COMe, 2.25 Å; other Cr–C 2.20—2.27 Å).[17]

Presumably the tendency to adopt the form (II) is much less when the substituent is OMe than when it is NR^2R^3 because the more electronegative oxygen does not stabilise the positive charge so well as the nitrogen. In fact, we have shown that the π-phenol complexes can deprotonate readily to give the η^5-oxo-cyclohexadienyl form.[4]

EXPERIMENTAL

All reactions were carried out under a protective atmosphere of nitrogen; however, none of the isolated complexes showed any signs of instability towards air. Microanalyses were carried out by the Department of Chemistry Microanalytical Service and are collected in Table 1; ^1H and ^{13}C n.m.r. spectra (Table 1) were measured on a Perkin-Elmer R-34 (at 220 MHz) and a JEOL PFT-100 spectrometer respectively. The aromatic amines and anisole were of commercial reagent grades. Typical preparations are illustrated below.

(NN-*Dimethyl*-p-*toluidine*)*pentamethylcyclopentadienylrhodium Hexafluorophosphate* (7a).—*NN*-Dimethyl-*p*-toluidine (62.3 mg, 0.5 mmol) was added to a solution of $[Rh(C_5Me_5)(MeCN)_3][PF_6]_2$[3] (300 mg, 0.5 mmol) in acetone (20 cm^3). After stirring for 5 h at 20 °C the clear yellow solution was evaporated to 2 cm^3 *in vacuo*. Diethyl ether was added to give yellow crystals of complex (7a) (279 mg, 84%) which were filtered off, washed with ether, and dried. All the rhodium–aniline complexes were prepared in this way.

(NN-*Dimethyl*-p-*toluidine*)*pentamethylcyclopentadienyliridium Hexafluorophosphate* (7b).—*NN*-Dimethyl-*p*-toluidine (67 mg, 0.58 mmol) was added to a solution of $[Ir(C_5Me_5)(Me_2CO)_3][PF_6]_2$ {made from $[Ir_2(C_5Me_5)_2Cl_4]$[3] 199 mg, 0.25 mmol} in acetone (20 cm^3). The initially orange solution was stirred for 18 h at 20 °C, the precipitate

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* Values for the free arenes were taken from ref. 18.

removed by centrifuging, and diethyl ether added to give white microcrystalline complex (7b) (309 mg, 82%) which was filtered off and dried. All the iridium complexes and the rhodium–anisole complex were prepared in this way.

X-*Ray Structure Determination of* [Rh(C_5Me_5)(PhNHMe)]-[PF_6]$_2$ (4a).—A single crystal was selected from a batch obtained by slow crystallisation of a sample of complex (4a) from acetone.

Crystal data. $C_{17}H_{24}F_{12}NP_2Rh$, $M = 635.22$, Orthorhombic, $a = 15.066(13)$, $b = 32.81(3)$, $c = 9.536(9)$ Å (obtained from a least-squares fit to the setting angles of 67 reflections centred manually), $U = 4\,713.4$, $D_m = 1.790$, $Z = 8$, $D_c = 1.76$ g cm^{-3}.

Systematic absences indicated that the space group was either *Pbnm* or *Pbn*2_1 (non standard settings of No. 62 and No. 33 respectively). Three-dimensional *X*-ray data were collected with the crystal mounted along the *c* axis using Mo-K_α radiation (graphite monochromator) and a Stoe STADI-2 diffractometer. 1478 Independent reflections were collected with $I_{obs.} \geqslant 3\sigma(I_{calc.})$. A Patterson function was calculated and examined initially to determine which of the two space groups was present. The [O, O, W] Harker line showed no peaks other than at the origin; this suggested that the space group was *Pbn*2_1 with two molecules per equivalent position. The positions of the two rhodium atoms were found from the Patterson function; their '*z*' co-ordinates were very similar and it was thought possible that the molecules may have crystallised in *Pbnm* with two molecules per equivalent special position, each lying across the minor plane. Both possible space groups were tried but eventually refinement in the centric space group was more sensible, although some disorder had to be included.

The remaining non-hydrogen atoms were found from a series of structure-factor calculations and Fourier syntheses. Block-diagonal least squares refinement reduced *R* to 0.109 at which stage a difference-Fourier synthesis showed some residual electron density close to the phosphorus atoms. This, together with high thermal parameters on the fluorine atoms, suggests some disordering of the hexafluorophosphate ions which was then included in the structure-factor calculations. Refinement continued using isotropic then anisotropic thermal parameters for all atoms and converged at $R = 0.065$.

The molecules are situated in the unit cell with all rhodium and phosphorus atoms lying in crystallographic mirror planes. The pentamethylcyclopentadienyl ring lies perpendicular to the plane with one carbon atom and its methyl substituent lying in the plane. The mirror plane is also perpendicular to the six-membered ring but passes through the midpoints of two opposite bonds so that disorder is implied. Difference-Fourier syntheses did not resolve the two sets of ring carbon atoms, however the atoms of the *N*-methyl substituent to the ring were only included in the structure-factor calculation as atoms of half population. The anisotropic thermal parameters must therefore to some extent reflect the slight change in position associated with the disorder in the ring carbon atoms. The overall geometry of the two cations is similar (Figure 2).

Atomic scattering factors were taken from ref. 19. Calculations were performed on the Sheffield University ICL 1906S computer using programs from the Sheffield *X*-ray System.

Atomic co-ordinates are listed in Table 3 and important bond lengths and bond angles in Table 2. Tables of observed and calculated structure factors, thermal parameters, and complete bond-length and bond-angle data for the structure are listed as Supplementary Publication No. SUP 22749 (30 pp.).*

TABLE 3

Positional atomic co-ordinates for [Rh(C_5Me_5)(PhNHMe)]-[PF_6]$_2$ (× 10^4, except Rh × 10^5) with estimated standard deviations in parentheses

Atom	*X*	*Y*	*Z*
Rh(A)	19 556(13)	40 395(7)	25 000(0)
Rh(B)	15 468(12)	18 016(7)	75 000(0)
P(A)	186(4)	2 519(2)	2 500(0)
P(B)	3 490(5)	−2(2)	7 500(0)
P(C)	158(5)	3 424(3)	7 500(0)
P(D)	677(6)	800(2)	2 500(0)
F(A1)	715(13)	2 117(6)	2 500(0)
F(A2)	−323(12)	2 927(6)	2 500(0)
F(A3)	814(7)	2 686(5)	3 658(15)
F(A4)	−448(7)	2 365(5)	3 641(14)
F(B1)	3 890(19)	391(7)	7 500(0)
F(B2)	2 896(27)	−261(18)	7 500(0)
F(B3)	2 854(13)	212(6)	6 386(23)
F(B4)	4 158(14)	−203(7)	6 515(25)
F(B5)	4 118(30)	72(14)	6 300(35)
F(B6)	1 847(27)	4 624(10)	6 518(40)
F(C1)	−355(29)	3 055(10)	7 500(0)
F(C2)	663(29)	3 778(10)	7 500(0)
F(C3)	740(13)	3 241(7)	6 429(20)
F(C4)	−364(11)	3 585(7)	6 363(20)
F(D1)	183(26)	431(10)	2 500(0)
F(D2)	920(38)	1 180(10)	2 500(0)
F(D3)	−6(14)	986(7)	3 357(23)
F(D4)	1 355(14)	629(8)	3 479(27)
F(D5)	1 174(27)	1 088(14)	3 540(39)
F(D6)	462(36)	530(16)	3 715(45)
C(A7)	2 943(15)	3 559(7)	2 500(0)
C(A8)	3 056(10)	3 805(6)	3 718(21)
C(A9)	3 271(9)	4 217(5)	3 266(18)
Me(A7)	2 772(21)	3 108(9)	2 500(0)
Me(A8)	3 011(14)	3 679(8)	5 239(26)
Me(A9)	3 430(13)	4 598(6)	4 178(25)
C(B7)	2 576(15)	2 265(9)	7 500(0)
C(B8)	2 693(10)	1 997(6)	6 288(23)
C(B9)	2 815(9)	1 575(5)	6 770(18)
Me(B7)	2 437(19)	2 711(9)	7 500(0)
Me(B8)	2 663(13)	2 153(7)	4 776(25)
Me(B9)	2 986(12)	1 225(6)	5 800(24)
C(A1,6)	983(12)	4 561(6)	3 229(24)
C(A2,5)	826(11)	4 176(5)	3 970(22)
C(A3,4)	622(10)	3 814(5)	3 229(18)
N(A)	1 082(19)	4 937(8)	3 538(35)
Me(A6)	1 249(21)	5 327(8)	2 814(37)
C(B1,6)	493(10)	1 331(6)	6 738(23)
C(B2,5)	403(10)	1 700(6)	6 013(23)
C(B3,4)	256(10)	2 075(5)	6 765(19)
N(B)	558(16)	926(10)	6 486(33)
Me(B6)	790(20)	557(8)	7 276(56)
Estimated positions (see text)			
C(A1)	1 030	4 538	3 253
C(A6)	935	4 585	1 796
C(B1)	549	1 325	6 730
C(B6)	436	1 337	8 254

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

REFERENCES

[1] Part 25, P. Espinet and P. M. Maitlis, *J. Organometallic Chem.*, 1979, **179**, 49.

[2] C. White and P. M. Maitlis, *J. Chem. Soc.* (*A*), 1971, 3322.

[3] C. White, S. J. Thompson, and P. M. Maitlis, *J.C.S. Dalton*, 1977, 1654.

[4] C. White, S. J. Thompson, and P. M. Maitlis, *J. Organometallic Chem.*, 1977, **127**, 415.

[5] P. M. Maitlis, *Accounts Chem. Res.*, 1978, **11**, 301.

[6] See, for example, S. Sternhell in ' Dynamic N.M.R. Spectroscopy,' eds. F. A. Cotton and L. A. Jackman, Academic Press, New York, 1975, p. 185.

[7] P. L. Pauson and J. A. Segal, *J.C.S. Dalton*, 1975, 1677.

[8] M. R. Churchill and S. W. Y. Ni, *J. Amer. Chem. Soc.*, 1973, **95**, 2150; M. R. Churchill, S. A. Julio, and F. A. Rotilla, *Inorg. Chem.*, 1977, **16**, 1137; W. Rigby, H. B. Lee, P. M. Bailey, J. A. McCleverty, and P. M. Maitlis, *J.C.S. Dalton*, 1979, 387; P. Espinet, P. M. Bailey, P. Piraino, and P. M. Maitlis, *Inorg. Chem.*, 1979, **18**, 2706.

[9] M. R. Churchill and F. R. Scholer, *Inorg. Chem.*, 1969, **8**, 1950.

[10] P. J. van Vuuren, R. J. Fletterick, J. Meinwald, and R. E. Hughes, *J. Amer. Chem. Soc.*, 1971, **93**, 4394.

[11] M. Mathew and G. J. Palenik, *Inorg. Chem.*, 1972, **11**, 2809.

[12] Yu V. Gatilov, N. G. Bokii, and Yu T. Struchkov, *J. Struct. Chem.*, 1975, **16**, 788.

[13] A. Mawby, P. J. C. Walker, and R. J. Mawby, *J. Organometallic Chem.*, 1973, **55**, C39.

[14] W. E. Silverthorn, *Adv. Organometallic Chem.*, 1975, **13**, 48 and refs. therein.

[15] O. L. Carter, A. T. McPhail, and G. A. Sim, *J. Chem. Soc.* (*A*), 1967, 228.

[16] A. Efraty and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1967, **89**, 3744.

[17] O. L. Carter, A. T. McPhail, and G. A. Sim, *J. Chem. Soc.* (*A*), 1966, 228.

[18] J. B. Stothers, ' Carbon-13 N.M.R. Spectroscopy,' Academic Press, New York, 1972.

[19] ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.