Pentamethylcyclopentadienyl-rhodium and -iridium Complexes. Part 32.[1] Reactions of Tri-μ-hydroxo-complexes with Aniline and Aliphatic Amines

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The complexes $[\{M(C_5Me_5)\}_2(OH)_3]OH$ (1, M = Rh; 2, M = Ir) react with aniline in the presence of PF_6^- or BF_4^- to give the μ-anilido-complexes $[\{M(C_5Me_5)\}_2(\mu\text{-}NHPh)(\mu\text{-}OH)_2]^+$. Models show that the anilido-ligand sits rigidly in a pocket between the metal atoms and the n.m.r. spectra indicate there to be no rotation about the C–N bond. Primary alkylamines react with (1) to give tris(amine) complexes $[Rh(C_5Me_5)(NH_2R)_3]^{2+}$ (R = n-propyl or benzyl) which immediately dissociate in solution. Reasons for the differences in behaviour of the two types of amines are discussed.

THE previous paper in this series[1] discussed the reaction of phenol with tri-μ-hydroxo-dirhodium complexes to give tri-μ-phenoxo-complexes, *e.g.* $[\{Rh(C_5Me_5)\}_2(OPh)_3]^+$. We now report on a related reaction with aniline, as well as reactions with n-propylamine and benzylamine.

RESULTS AND DISCUSSION

Reactions with Aniline.—Reaction of the hydroxo-hydroxide complexes (1) and (2)[2,3] with aniline in water in the presence of KPF_6 gave crystalline precipitates (3a) and (4) respectively. A similar material (3b) was obtained by the reaction of (1) and aniline in the presence of $NaBF_4$ (see below). Attempts were made to carry out an *X*-ray structure determination on some of these crystals but in all cases the preliminary photographs were blurred and indistinct, indicating severe disorder.

Microanalytical and i.r. data were in agreement with (but did not prove) the complexes (3) and (4) containing the cation $[\{M(C_5Me_5)\}_2(NHPh)(OH)_2]^+$, but the key structural evidence came from the ^1H and ^{13}C n.m.r. spectra. The complexes decomposed slowly in all solvents in which they dissolved, but reasonable spectra could be obtained from freshly made up solutions.

The ^1H n.m.r. spectra of all three complexes in $[^2H_6]$-acetone showed a singlet at *ca.* δ 1.40 p.p.m. due to C_5Me_5, a multiplet near δ 7 (phenyl) and another singlet at *ca.* δ 2.9 due to NH and OH. The experimentally found intensity ratios were 30 : 6 : 4 for (3a) or (4) and 30 : 5 : 6 for (3b), the i.r. spectrum of which indicates it to contain some water of crystallisation. The intensity ratios expected are 30 : 5 : 3 for the structures shown for (3a) or (4) and 30 : 5 : 7 for (3b) if it has two water molecules of crystallisation.

We propose the formulation with a singly deprotonated aniline bridging the two metals because the i.r. spectra of these complexes showed only a single band ascribable to ν(NH). By contrast, complexes containing RNH_2 coordinated to the metal showed two ν(NH) bands in this region (see below).

One surprising and unusual feature of the ^{13}C n.m.r. spectra of (3a) and (4) was that all the carbons of the aniline phenyl ring were in different environments, in other words that six resonances could be ascribed to the liganded aniline.† None of these aromatic resonances in (3a) showed any doubling arising from coupling to Rh; hence there is no π (or σ) metal–carbon binding. The asymmetry of the phenyl group in the liganded aniline was confirmed by the ^1H n.m.r. spectrum of (3b) (at 400 MHz) which showed *five* distinct phenyl hydrogens (at δ 6.95, 7.21, 7.25, 7.36, and 7.61).

This contrasts with the situation in the tri-μ-phenoxo-complexes where the plane of symmetry perpendicular to the aromatic ring is retained and only four phenyl carbon resonances are seen in the ^{13}C spectrum.[1] Alternatively, the second plane of symmetry in the phenoxo-complexes that is inferred from the n.m.r. spectra may arise from a rotation about the Ph–O bond which is fast on the n.m.r. timescale.

The data on (3) and (4) are consistent with a very rigid structure in which the aniline NH bridges the two rhodiums and where the phenyl ring fits into a pocket between the $Rh(C_5Me_5)$ moieties in such a way that rotation about the C–N bond is strongly inhibited.

Since no crystal-structure determination was possible, a computer model of the structure of (4) was constructed. Parameters derived from the previously determined[3] structure of the tri-μ-hydroxo-iridium complex $[\{Ir(C_5Me_5)\}_2(OH)_3]O_2CMe\cdot 14H_2O$ and normal van der Waals radii were used and one μ-hydroxo-group was replaced by an N-bonded anilide of normal geometry (sp^3 at N). Inspection of the model showed (*i*) that when the C_6H_5N plane was parallel to the C_5Me_5 rings there were *no* significant steric interactions and (*ii*) that there were *very severe* steric constraints to the C_6H_5N plane being perpendicular to the C_5Me_5 planes. There were particularly severe interactions between the hydrogens on the phenyl and the methyl hydrogens of the C_5Me_5 ligands.

Hence the anilide can only act as a bridging ligand when the phenyl is in a parallel orientation and rotation about the C–N bond would be extremely difficult. In the parallel orientation one edge of the phenyl is facing inwards (towards the M–M axis) and the opposite edge outwards. Hence the two halves of the phenyl ring are different; this would account for the multiplicity of

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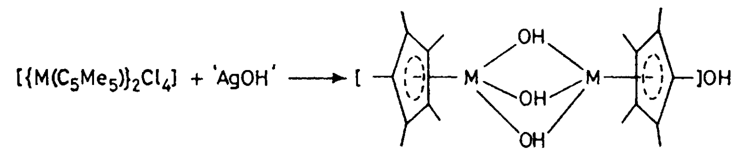
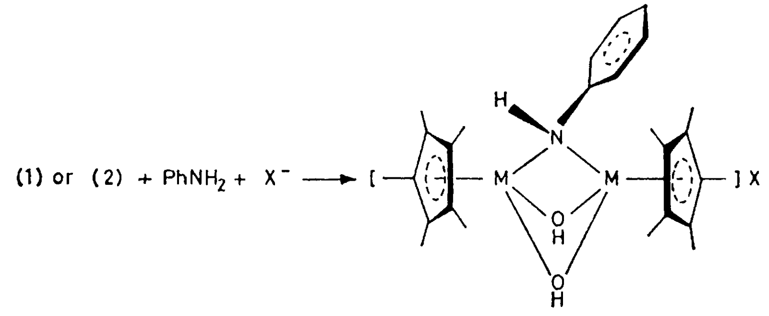
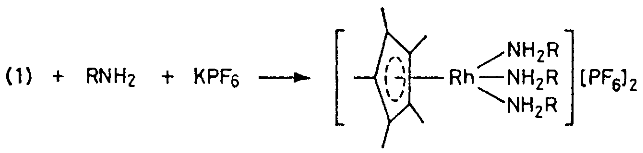
† In addition, some samples of (3a) and (4) showed resonances due to free aniline, present as an impurity.



(1) M = Rh
(2) M = Ir



(3a) M = Rh, X = PF_6
(3b) M = Rh, X = BF_4
(4) M = Ir, X = PF_6



(5) R = Pr^n
(6) R = $PhCH_2$

signals shown by the ^{13}C and the high resolution ^{1}H spectra.

It is also interesting to note that here, as in the phenoxy-complexes, two quite different types of binding of the metal centre to the ligand are possible. Thus these monocationic N-bonded anilido-complexes may be contrasted with the dicationic π-bonded (η^5) aniline complexes $[Rh(C_5Me_5)(C_6H_5NH_2)][PF_6]_2$ previously reported.[4] We have so far not discovered any straightforward route from the N- to the π-bonded complexes, or *vice-versa*.

Reactions with n-Propylamine and Benzylamine.—By contrast, addition of either n-propylamine or benzylamine to an aqueous solution of $[\{Rh(C_5Me_5)\}_2(OH)_3]OH$ (1) containing some KPF_6 gave a yellow precipitate. Both these materials were very unstable; for example, they decomposed rapidly in solvents in which they were soluble (such as thf or acetone) and could therefore not be recrystallised. N.m.r. investigations were not feasible for the same reason. Microanalyses agreed with the formula $[Rh(C_5Me_5)(NH_2R)_3][PF_6]_2$ and the structures (5) and (6) are suggested. In support is the observation that both show two ν(NH) bands (asymmetric and symmetric) in the i.r. [3 323m, 3 285m for (5) and 3 350m, 3 293m cm^{-1} for (6)] consistent with the presence of co-ordinated RNH_2– rather than $RNH\langle$.[5] Other bands in the i.r. spectra of (5) and (6) are also found in the two parent amines.

These complexes are similar to the tris(ammine) complex $[Rh(C_5Me_5)(NH_3)_3][PF_6]_2$ (7) which has been made by the action of liquid ammonia on $[\{Rh(C_5Me_5)\}_2Cl_4]$.[6] The complex (7) and its analogue $[Ru(C_6H_6)(NH_3)_3]^{2+}$ can also be obtained by deprotonation of ammonium salts (especially NH_4PF_6), *e.g.* equation (1).[7]

$$[\{Ru(C_6H_6)\}_2(OH)_3]Cl + NH_4PF_6 \longrightarrow [Ru(C_6H_6)(NH_3)_3][PF_6]_2 \quad (1)$$

The tris(ammine) salt (7) is however appreciably more stable than (5) or (6). This may well be due to the inter-ligand repulsions between the R groups of the three amines and the C_5Me_5 methyls being much greater in (5) or (6) than in (7) where R = H. We have previously observed substantial steric effects in the synthesis of tris-(phosphine) and -(phosphite) complexes,[8] even though these ligands bind more strongly to $Rh(C_5Me_5)$ than do amines.

The reason for the difference in binding of the aliphatic and aromatic amines we believe to lie in the relative basicities and acidities of the different types of primary amines. Ammonia and aliphatic amines are good Brønsted bases and also appear to act in the same way towards $Rh(C_5Me_5)$. Aniline, however, is a weaker base but a stronger acid than either ammonia or aliphatic amines [9] and so in that case a stronger complex is formed with the deprotonated anilido-ligand than with aniline itself.

Although complexes containing amines such as aniline are commonplace, for example $[\{Rh(C_5Me_5)\}_2Cl_4]$ forms $[Rh(C_5Me_5)Cl_2(NH_2C_6H_4CH_3\text{-}\mathit{p})]$,[10] complexes containing deprotonated amines are more rare. However, rhodium does form complexes with deprotonated ethylenediamine, *e.g.* $[Rh(NH_2CH_2CH_2NH)_3]$,[11] and an anilide complex of platinum has been reported.[12]

EXPERIMENTAL

Microanalyses were determined by the University of Sheffield Microanalytical Service; n.m.r. spectra were measured on Perkin-Elmer R-12B (60 MHz, ^1H), Bruker WH-400 (400 MHz, ^1H; courtesy of the S.R.C. National Service), and JEOL PFT-100 (^{13}C) spectrometers.

$[\{Rh(C_5Me_5)\}_2(NHPh)(OH)_2][PF_6]$ (3a) and $[\{Rh(C_5Me_5)\}_2(NHPh)(OH)_2][BF_4]\cdot 2H_2O$ (3b).—Aniline in water (4 cm^3, 2.5% w/v) was added to a solution of complex (1) (0.2 g) and KPF_6 (0.1 g) in water (20 cm^3) and the solution was set aside (20 °C, 16 h). The orange crystalline solid that had formed was filtered off, washed with water, and dried to give complex (3a) (0.13 g) (Found: C, 43.7; H, 5.5; N, 2.7.* $C_{28}H_{38}F_6NO_2PRh_2$ requires C, 41.8; H, 5.1; N, 1.9%). ^1H N.m.r. (60 MHz, [$^2H_6$]acetone): δ (p.p.m.) 1.38 (s, C_5Me_5), 2.93 (s, OH, NH), and 7.0 (m, Ph). ^{13}C N.m.r.* ([$^2H_6$]-acetone): δ (p.p.m.) 8.4 ($C_5\mathit{Me}_5$), 90.3 [d, C_5Me_5, J(C-Rh) 10 Hz], 122.0, 122.6, 123.3 (Ph *o*-, *o′*-, and *p*-), 128.0, 129.8 (Ph *m*-, *m′*-), and 155.4 (Ph, *i*-). I.r.: ν(OH) 3 635w, 3 565ms, 3 460w, 3 400w, 3 340w, br, ν(NH) 3 215wm, ν(CN) 1 237s, ν(PF) 840vs cm^{-1}.

The tetrafluoroborate (3b) (0.10 g) was prepared similarly but using $NaBF_4$ (0.1 g) in place of KPF_6 (Found: C, 42.8; H, 6.1; N, 1.9. $C_{38}H_{38}BF_4NO_2Rh_2\cdot 2H_2O$ requires C, 43.1; H, 5.8; N, 1.9%). ^1H N.m.r. (400 MHz, [$^2H_6$]acetone): δ (p.p.m.) 1.39 (s, C_5Me_5), 2.96 (s, NH, OH), 6.95 [tt, H_p $J(H_p\text{–}H_m)$ 7, $J(H_p\text{–}H_o)$ 1], 7.21 [dt, H_m, $J(H_m\text{–}H_p)$ 7, $J(H_m\text{–}H_o)$ 7, $J(H_m\text{–}H_m)$ 1], 7.25 [dt, H_m, couplings as for H_m], 7.36 [dd, H_o, $J(H_o\text{–}H_m)$ 7, $J(H_o\text{–}H_p)$ 1 Hz], 7.61 [dd, $H_{o'}$, couplings as for H_o]. I.r.: ν(OH) 3 593mw, 3 503ms, 3 480m, 3 380w, br, ν(NH) 3 218mw, ν(CN) 1 227, ν(BF) 1 092, 1 073, 1 050, 1 035, 1 010 (all s) cm^{-1}.

$[\{Ir(C_5Me_5)\}_2(NHPh)(OH)_2][PF_6]$ (4).—This complex (0.15 g) was obtained from (2) (0.1 g) in the manner described for complex (3a) (Found: C, 34.3; H, 4.3; N, 1.6.* $C_{28}H_{38}F_6Ir_2NO_2P$ requires C, 33.7; H, 4.1; N, 1.5%). ^1H N.m.r. (60 MHz, [$^2H_6$]acetone): δ (p.p.m.) 1.40 (s, C_5Me_5), 2.90 (s, OH, NH), 7.00 (m, Ph). ^{13}C N.m.r. ([$^2H_6$]acetone): δ (p.p.m.) 8.9 ($C_5\mathit{Me}_5$), 81.8 (C_5Me_5), 122.4, 122.4, 123.4 (Ph *o*, *o′*, and *p*, two coincident), 127.8, 129.5 (Ph *m*, *m′*), and 153.3 (Ph *i*).* I.r.: ν(OH) 3 663mw, 3 563s, 3 400w, br, ν(NH) 3 300wm, ν(CN) 1 222s, ν(PF) 840vs cm^{-1}.

$[Rh(C_5Me_5)(NH_2Pr^n)_3][PF_6]_2$ (5).—A solution of complex (1) (0.2 g) and n-propylamine (0.1 g) in water (15 cm^3) was stirred (25 °C, 1 h). A solution of KPF_6 (0.1 g) in water (5 cm^3) was then added; this precipitated the yellow solid (5) (0.18 g) which was filtered off, washed, and dried (Found: C, 32.7; H, 6.3; N, 6.7. $C_{19}H_{42}F_2N_3P_2Rh$ requires C, 32.4; H, 6.0; N, 6.0%). I.r.: ν(NH) 3 323m, 3 285m, ν(PF) 840vs cm^{-1}; n-$C_3H_7NH_2$ shows ν(NH) 3 370m and 3 285m cm^{-1}.

$[Rh(C_5Me_5)(PhCH_2NH_2)_3][PF_6]_2$ (6).—This complex (0.18 g) was obtained in an identical manner from (1) and benzylamine (0.1 g) (Found: C, 39.1; H, 4.6; N, 5.4. $C_{31}H_{42}F_2N_3P_{12}Rh$ requires C, 39.6; H, 5.0; N, 5.0%). I.r.: ν(NH) 3 350m, 3 293m, ν(PF) 840vs cm^{-1}; $PhCH_2NH_2$ shows ν(NH) 3 377m and 3 298m cm^{-1}.

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* The microanalysis and ^{13}C n.m.r. spectrum (at δ 115.0, 117.2, 129.5, and 149.4) showed the presence of a small amount of free aniline.