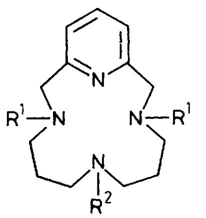
Formation of Ethyl- and Hydrido-iridium(III) Complexes from the Reaction of Hydrated Iridium(III) Chloride with a Pyridine-containing Tetra-azamacrocycle in Aqueous Ethanolic Solution. Crystal Structure of *trans*-[IrCl(Et)L^1][PF_6] {L^1 = 3,7,11-trimethyl-3,7,11,17-tetra-aza-bicyclo[11.3.1]heptadeca-1(17),13,15-triene}

Peter Moore,* Hadi A. A. Omar, Nathaniel W. Alcock, and Graham A. Pike
Department of Chemistry, University of Warwick, Coventry CV4 7AL, U.K.

Reaction of a pyridine-containing tetra-azamacrocycle, 3,7,11-trimethyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene, L^1, with $IrCl_3 \cdot 3H_2O$ in refluxing aqueous ethanolic solution gives a mixture of hydrido-iridium(III) complexes, together with substantial amounts of *trans*-$[IrCl(Et)L^1]^+$, as shown by NMR measurements, FAB MS, and the single crystal *X*-ray structure of the ethyl complex.

It has recently been found that the pyridine-containing tetra-azamacrocycle L^2 reacts with hydrated iridium(III) chloride in aqueous ethanolic solution to give *cis*-$[IrCl(H)L^2]^+$ ion.[1] Whilst studying an analogous reaction of L^1 with $IrCl_3 \cdot 3H_2O$ in refluxing ethanol, three isomeric hydrido-iridium(III) complexes were observed to form, as well as substantial amounts of *trans*-$[IrCl(Et)L^1]^+$ ion. To L^1 (0.14 g, 0.5 mmol; prepared as described previously[2,3]) in ethanol (100 cm^3) and water (100 cm^3) was added $IrCl_3 \cdot 3H_2O$ (0.25 g, 0.71 mmol). Upon heating the mixture under reflux for 2 h, the formation of $[IrCl(H)L^1]^+$ ions was detected by FAB MS (*m/z* 505), along with a small amount of $[IrCl(C_2H_5)L^1]^+$ (*m/z* 533). A ^1H NMR spectrum in CD_3NO_2 shows the formation of three isomeric hydrido complexes with characteristic hydride resonances at δ −17.74, −22.95, and −25.17. The presence of the ethyl complex is also evident in the ^1H NMR spectrum, with resonances from the ethyl group at δ 0.07 (t, 3H) and 2.37 (q, 2H), and in a DEPT ^{13}C NMR spectrum with resonances at δ −3.72 (CH_2) and 16.60 (Me). After refluxing for 24 h, the concentration of the ethyl complex increased markedly as shown by the FAB mass spectrum; the solution was filtered to remove a black precipitate (Ir metal), concentrated to 10 cm^3 with a rotary evaporator, and $[NH_4][PF_6]$ (0.24 g, 1.47 mmol) added to precipitate a yellow solid (0.125 g). This was analysed by ^1H NMR spectroscopy and found to contain the ethyl complex and the three hydrido species in the molar ratio 4.95 (ethyl): 1 (hydride at δ −17.74): 2.7 (hydride at δ −22.95): 2.4 (hydride at δ −25.17). Prolonged heating under reflux for 5 days results in decomposition of the ethyl complex, and only the two hydrido species with resonances at δ −22.95 and −25.17 remain (relative areas 2.2 : 1 respectively).† The preparation was repeated in aqueous deuterioethanol, and FAB mass spectra reveal the formation of $[IrCl(D)L^1]^+$ (*m/z* 506) and $[IrCl(C_2D_5)L^1]^+$ (*m/z* 538). Recrystallisation of the mixture of ethyl- and hydrido-complexes by slow evaporation of a saturated nitromethane solution gives pale yellow crystals of the ethyl complex, *trans*-$[IrCl(Et)L^1][PF_6]$, suitable for crystallography.‡ Figure 1 shows the cation geometry, with the ethyl group *trans* to the chloride ion. The Ir–C bond length [2.136(11) Å] is similar to that found in *mer*-$[IrBr_2(Et)(PMe_3)_3]$ (2.123 Å).[4] The *trans*-influence of the ethyl group is evident from the long Ir–Cl bond length of 2.536(3) Å, compared to the much shorter Ir–Cl bond length of 2.393(4) Å found in the *cis*-$[IrCl(H)L^2]^+$ ion where the chloride is in a *trans*-position to the pyridine ring.[1] The Ir–N bond lengths are close to 2.14 Å, with the exception of the bond to the pyridine N atom which is significantly shorter [1.950(7) Å]. This is as expected by comparison with $[NiX(L^1)]^{n+}$ ions ($X = Cl^-$, n = 1; X = dimethyl sulphoxide, n = 2) and *cis*-$[IrCl(H)L^2]^+$, where the metal–N bonds to pyridine are significantly shorter than to the other N atoms.[1,2] The iridium is close to the plane formed by the four N atoms, being displaced only 0.03 Å in the direction of the ethyl group. The N(1)–Ir–C(1A)–C(2A) torsion angle is close to zero, with the methyl of the ethyl group above the Ir–N(1) bond, as far away as possible from the repulsive effect of the three N-methyl groups which are on the same side of the macrocyclic plane as the ethyl group.

The formation of an ethyliridium(III) complex is perhaps surprising in view of its apparent absence during the analogous



L^1; $R^1 = R^2$ = Me
L^2; R^1 = H, R^2 = Me
L^3; $R^1 = R^2$ = H

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† Elemental analyses (CHN) consistent with the formula given were obtained.

‡ *Crystal data* for $C_{18}H_{33}ClF_6IrN_4P$, pale yellow crystals, M = 678.11, monoclinic, space group $P2_1/c$, a = 7.3997(31), b = 23.580(13), c = 13.164(68) Å, β = 95.242(38)°, U = 2287 $Å^3$, Z = 4, D_c = 1.969 g cm^3, λ = 0.71069 Å, μ = 60.6 cm^{-1}, T = 291 K, $F(000)$ = 1328, R = 0.043 (R_w = 0.047), 4032 independent reflections, 3250 with $I/\sigma(I) \geqslant 2.0$ used in refinement. Data were collected using graphite monochromated Mo-K_α radiation in the ω–2θ mode, to $2\theta_{max.}$ = 50°. Three standard reflections were monitored every 200 reflections, and showed slight changes during data collection; the data were rescaled to correct for this. Reflections were processed using profile analysis, and were corrected for Lorentz, polarisation and absorption effects, the last by the Gaussian method. Heavy atoms were located by the Patterson interpretation section of SHELXTL, and light atoms then found on successive Fourier syntheses. Anisotropic temperature factors were used for all non-H atoms. Hydrogen atoms were given fixed isotropic temperature factors, U = 0.07 $Å^3$. Those defined by the molecular geometry were inserted at calculated positions and not refined; methyl groups were treated as rigid CH_3 units, with their initial orientation taken from the strongest H-atom peaks on a difference Fourier synthesis. Final refinement was on F by least-squares methods, refining 280 parameters. Largest positive and negative peaks on a final difference Fourier synthesis were of height 1.26 and −1.13 e $Å^{-3}$. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with g = 0.0014 was used and shown to be satisfactory by a weight analysis. Computing was done with SHELXTL PLUS.[5] Final atomic co-ordinates, bond lengths and angles, and thermal parameters, have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

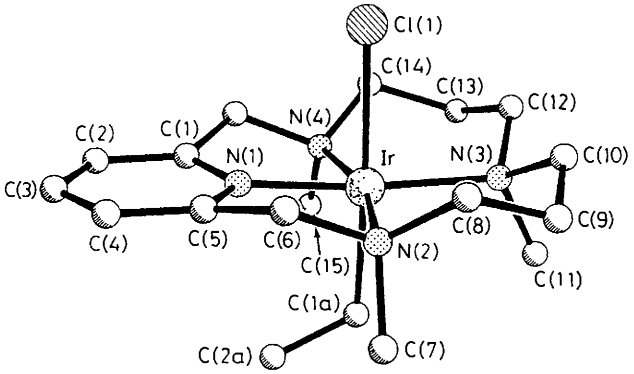

Figure 1. Structure of the *trans*-[IrCl(Et)L^1]$^+$ cation with the numbering scheme adopted. Selected bond lengths (Å): Ir–Cl(1) 2.536(3), Ir–N(1) 1.950(7), Ir–N(2) 2.147(8), Ir–N(3) 2.131(8), Ir–N(4) 2.139(8), Ir–C(1A) 2.136(11). Selected bond angles (°): Cl(1)–Ir–N(1) 84.5(2), Cl(1)–Ir–N(2) 91.4(2), Cl(1)–Ir–N(3) 89.8(2), Cl(1)–Ir–N(4) 89.8(2), N(1)–Ir–N(2) 81.9(3), N(1)–Ir–N(3) 174.3(3), N(1)–Ir–N(4) 82.5(3), N(2)–Ir–N(3) 98.5(3), N(2)–Ir–N(4) 164.1(3), N(3)–Ir–N(4) 97.4(3), Cl(1)–Ir–C(1A) 176.8(3), N(1)–Ir–C(1A) 92.5(3), N(2)–Ir–C(1A) 89.2(3), N(3)–Ir–C(1A) 93.1(3), N(4)–Ir–C(1A) 88.8(3). C(2A)–C(1A)–Ir–N(1) torsion angle 0.6°.

reaction of L^2.[1] However, we have observed that the reaction of $IrCl_3{\cdot}3H_2O$ with the parent macrocycle, L^3, in refluxing aqueous ethanol also gives small amounts of ethyliridium(III) and hydrido-iridium(III) species, although the major product in this case was found to be [$IrCl_2$(L^3)]$^+$. Formation of small amounts of [IrCl(Et)(L^3)]$^+$ is evident from the FAB mass spectrum after refluxing for 2 h (*m*/*z* 491); also in the ^{1}H NMR spectrum (CD_3NO_2) evidence is found for small amounts of two ethyliridium(III) species [methyl resonances of the ethyl groups at δ 0.20 (t, 3H; species 1) and −0.16 (t, 3H; species 2)], as well as hydrido-complexes with resonances at −24.37, −24.47 (major hydrido resonance), and −24.49. It seems likely, therefore, that a small amount of an ethyliridium(III) species may also be formed during the analogous reaction of L^2.

In the absence of further evidence, one can only speculate as to how the ethyl complexes form, but in view of the observed formation of hydrido-complexes, one feasible mechanism would be insertion of ethene into an Ir–H bond (*i.e.*, migration of hydride to co-ordinated ethene), presumably through a *cis*-species of the type reported for L^2.[1] The ethene probably forms by an iridium(III) catalysed dehydration of co-ordinated ethanol, analogous to the acid catalysed dehydration of ethanol. An alternative mechanism for the formation of [IrCl(Et)L^1]$^+$ would be oxidative addition of ethyl chloride to a macrocyclic iridium(I) complex, although addition of excess ethyl chloride to the reaction mixture has not been found to increase the yield of [IrCl(Et)L^1]$^+$ ion as one might expect in this case. Therefore, we favour the insertion mechanism.

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