Low-energy Photochemical Reactions of the Tetrakis(methyl isocyanide)iridium(I) Cation and some Oxidative Additions of a Stable Complex of Five-co-ordinate Iridium(I)

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Summary The deep blue cation $[Ir(MeNC)_4]^+$ associates with monodentate ligands L when irradiated with visible light and some of the products $[IrL(MeNC)_4]^+$ dissociate thermally in the dark back to $[Ir(MeNC)_4]^+$ and L; the very stable five-co-ordinate cation $[Ir(MeNC)(dppe)_2]^+$ is formed by photosubstitution and it undergoes oxidative additions without loss of any of its existing ligands.

METHYL isocyanide acts as a powerful monodentate ligand towards transition metals in low and intermediate oxidation states.[1,2] Thus, blue-black $[Ir(MeNC)_4]X$ (I; X = Cl; ν_{CN} 2202 vs cm^{-1}, τ 6·00 s, Me, in D_2O) was isolated (80%) from the reaction of *trans*-$IrCl(CO)(PPh_3)_2$ and excess MeNC. Other salts (I; X = PF_6, BPh_4, I) were obtained by metathesis. They were oxidised by air almost at once even as solids, and in solution absorbed one mol of O_2 in the dark to form orange adducts. Complex salts $[Ir(RNC)_4]X$ were reported previously for R = *p*-tolyl[1] and Bu^t,[3] but their properties were not described.

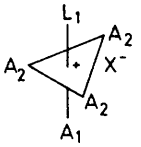
In the absence of oxygen the salts (I) gave intensely blue solutions in various solvents (S) (λ_{max} 610 ± 20 nm; ϵ 22,000). These solutions were stable for several days in the dark and in the cold but turned red or orange in light within seconds to minutes depending on concentration (λ_{max} 366 ± 6 and 418 ± 2 nm). This was observed for (I) when (X = Cl; S = MeOH), (X = BPh_4; S = Me_2CO, MeCN, Me_2SO, and $HCONMe_2$), and (X = PF_6; S = MeCN, Me_2SO, and $HCONMe_2$). In some cases the change was reversible. When the irradiated red solution of (I, X = Cl) in MeOH was stored in the dark it went blue in 6 days at 25° and in 20 min at 90°C. Only *aqueous* solutions were stable to light, but a slow thermal reaction gave $[MeNH_3]$ Cl and an insoluble carbonyl. The photochemical change was accompanied by slight but definite changes in the n.m.r. at 60 and 100 MHz. The singlet due to the equivalent methyl groups in (I) broadened (X = BPh_4, S = Me_2CO) or split into a number of closely spaced resonances (for X = BPh_4, S = MeCN: τ 6·29, 6·32, and 6·36; for X = Cl and S = MeOH: τ 5·90, 5·91, 5·93, 5·98, and 6·03). There were no other peaks in the range τ 0—50 and in particular the characteristic triplet of free methyl isocyanide at τ 6·92 (in CD_3CN) was absent, ruling out both photodissociation and photosubstitution. The slightly different methyl environments (A_1—A_4, A = MeNC) responsible for the resonances at $\tau \sim 6$ are consistent with a mixture of the trigonal bipyramidal solvates (IIa and IIb, L = S). We therefore suggest that the system presents a photochromic equilibrium between the four-co-ordinate blue cation of (I) and the five-co-ordinate orange-red solvates (II, L = S):

$$[\mathrm{Ir(MeNC)_4}]^+ + \mathrm{L} \underset{\text{heat}}{\overset{h\nu}{\rightleftharpoons}} [\mathrm{IrL(MeNC)_4}]^+ \qquad (1)$$

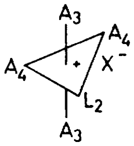
Aqueous solutions of (I, X = Cl) did not react with L = MeNC or CO in the dark, but the mixture turned orange in both cases when exposed to light. When L = MeNC the n.m.r. spectrum showed singlets at τ 6·00 and 6·10 (intensity ratio 2:3) corresponding to axial and equatorial isocyanides in $[Ir(MeNC)_5]^+$ (II, L = A = MeNC) This species decomposed on prolonged irradiation, but could be precipitated as $[Ir(MeNC)_5]BPh_4$. When L = CO the orange solution had singlets at τ 5·97 and 6·07 (intensity ratio 1:3) corresponding to A_1 and A_2 in (IIa) and at τ 6·20 and 6·25 (intensity ratio 1:1) corresponding to A_3 and A_4 in (IIb). The isomers were present in equal amounts. Orange $[Ir(CO)(MeNC)_4]BPh_4$ was precipitated by $NaBPh_4$ (ν_{CN} at 2253sh, 2215vs, 2183vs; ν_{CO} at 2010s), but addition of $NaClO_4$ resulted in evolution of CO even under 2 atm of carbon monoxide. A mixture of $[Ir(CO)(MeNC)_4]ClO_4$ and (I; X = ClO_4) separated, and the remaining carbon monoxide was lost in refluxing butanone under argon to give blue-black (I; X = ClO_4).

The forward reactions in equation (1) (L = S, CO, MeNC) are, to our knowledge,[4,5] the first examples of the photochemical formation of a metal–ligand bond (photo-association). The possibility had been recognised previously.[4] A possible mechanism could proceed through an essentially metal to ligand charge transfer making the metal centre in the excited complex more susceptible to nucleophilic attack by L. In some systems (*e.g.* L = MeOH) the ground state of the product might be unstable but fairly inert, resulting in slow thermal dissociation.

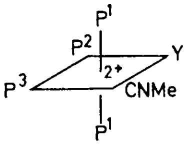
There was no reaction between (I) and $Ph_2PCH_2CH_2PPh_2$ (dppe) in the dark, but immediate photosubstitution occurred in light to give yellow $[Ir(MeNC)(dppe)_2]^+$ (III). This was isolated as the perchlorate (ν_{CN} 2124s cm^{-1}) and was also obtained from $[Ir(CO)(dppe)_2]^+$ and MeNC. Surprisingly, the CH_3 signal at τ 7·19 was a quintet, ^5J(P–H) 1·6 Hz, due to long range coupling to four ^{31}P nuclei. Most five-co-ordinate d^8 complexes lose a ligand in oxidative additions[3,6] but in (III) all five donor atoms are held tenaciously and are retained. Addition of Cl_2, I_2, HCl, and $HgCl_2$ gave doubly charged cations $[IrY(MeNC)(dppe)_2]^{2+}$ (IV; Y = Cl, I, H, and HgCl respectively), which formed hygroscopic crystalline salts with ClO_4^-, BF_4^- or BPh_4^-.† The hydride resonance of (IV, Y = H) at τ 20·7 was a doublet of a doublet of triplets, consistent with configuration (V) [$J(P^1–H)$ 15·6 Hz, $J(P^2–H)$ 10·2 Hz, and $J(P^3–H)$ 117 Hz]. The very broad methylene multiplet in (IV) compared to (III) suggests configuration (V) for the other adducts also. The C ≡ N stretch in (IV) was 110—125 cm^{-1} higher than in (III). Addition of H_2, O_2, SO_2, and C_3H_5I also occurred under mild conditions and is under study. MeI and MeCOCl did not react.



(IIa)



(IIb)



(V)

Whereas $PtCl_2(MeNC)(PR_3)$ reacts readily with alcohols to yield carbene complexes,[7] (III) was recovered unchanged after heating in methanol to 100° for 48 h, and after several weeks it was oxidised to Ir^{III}. Reaction of $[Ir(MeNC)_3(PPh_3)_2]^+$ with methanol is reported to yield $[Ir(OMe)(MeNC)_3(PPh_3)_2]^{2+}$ rather than a carbene.[13] Similarly, $[Pt(MeNC)_4]^{2+}$ (ν_{CN} 2290 cm^{-1}) reacts immediately and exothermically with hydrazine to give Chugaev's cation[2] whereas the isoelectronic $[Ir(MeNC)_4]^+$ (ν_{CN} 2202 cm^{-1}) did not react at all. Since the C≡N stretching frequency in the reactive isocyanides of Pt^{II} [2,7] is *ca.* 100 cm^{-1} higher than in the inert isocyanides of Ir^I it appears that the reaction with alcohols and amines to form carbenes is a property of isocyanide co-ordinated as a σ-donor but not as a π-acceptor.

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† Elemental analyses for all the compounds described [except (I)] were within ±0·3% of calculated. Compounds (I) were characterised by physical measurements only.

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