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Photoinduced isomerisation of the iridium(III) complex *trans,mer*-$[IrCl_2(CN)(PEt_2Ph)_3]$ to the *fac* and the *cis,mer* isomers

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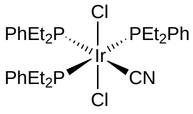
The chloride ligand *trans* to PEt_2Ph in *mer*-$[IrCl_3(PEt_2Ph)_3]$ has been found to be labile and readily displaced by cyanide ion in methanol to give *trans,mer*-$[IrCl_2(CN)(PEt_2Ph)_3]$ as the only isomer. The *trans,mer* isomer may also be synthesized by treating *trans,mer*-$[IrCl_2(H_2O)(PEt_2Ph)_3][ClO_4]$ with cyanide ions. Irradiation of this isomer in dichloromethane with visible white light led initially to a mixture of the *trans,mer* isomer with the *fac* and *cis,mer* isomers, while extended irradiation gave almost exclusively the *cis,mer* isomer with none of the *fac* or *trans,mer* forms remaining. This contrasts with the visible irradiation of *mer*-$[IrCl_3(PEt_2Ph)_3]$ which gave exclusively the *fac* isomer. Reactions were followed by ^{31}P-{^1H} and ^{13}C-{^1H} NMR spectroscopy of ^{13}CN-enriched samples and by Fourier-transform IR spectroscopy at around 2000 cm^{-1}. The crystal structures of the *trans,mer* and *cis,mer* isomers of $[IrCl_2(CN)(PEt_2Ph)_3]$ have been determined. During the photolysis a cyano-bridged species derived from the *fac* isomer, probably *fac,fac*-$[(PhEt_2P)_3Cl_2Ir(\mu\text{-}CN)IrCl(CN)(PEt_2Ph)_3]Cl$, is observed as an intermediate but was not isolated. This salt disappears on extended irradiation. Addition of an excess of $[N(PPh_3)_2]Cl$ totally suppressed the formation of the μ-CN species, consistent with the formula given, while only slightly affecting the rate of conversion of the *trans,mer* into the *fac* and *cis,mer* isomers on irradiation.

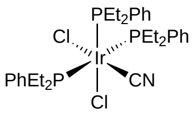
Chloroiridic acid reacts with PEt_2Ph in refluxing ethanol to give good yields of bright yellow crystals of *mer*-$[IrCl_3(PEt_2Ph)_3]$ with a low yield of the *fac* isomer being deposited later from the mother-liquor.[1] The geometry of the *mer* isomer is clearly apparent from the ^{31}P-{^1H} NMR spectrum which shows a doublet for the two mutually *trans* PEt_2Ph ligands and a triplet for the unique PEt_2Ph *trans* to Cl. The complex *mer*-$[IrCl_3(PEt_2Ph)_3]$ is light sensitive and irradiation of solutions in dichloromethane or other solvents with visible white light from a fluorescent lamp leads to the insoluble colourless *fac* isomer in high yield (96%)[2] and this is probably the origin of the *fac* isomer from the mother-liquor in the original synthesis of the *mer* isomer.[1] The corresponding orange rhodium complex *mer*-$[RhCl_3(PEt_2Ph)_3]$[3] also isomerises to the yellow *fac* isomer on irradiation but longer times of irradiation are needed in this case. It was reported that neither the nature of the solvent (benzene, acetone, chloroform, dichloromethane) nor the concentration of the iridium complex has any significant effect on the rate of isomerisation,[2] although we have observed slightly slower reactions at higher concentrations. It has also been shown that irradiation promotes phosphine exchange and therefore a possible mechanism is the expulsion of one of the tertiary phosphines, probably one of the two mutually *trans* PEt_2Ph ligands, from an electronically excited complex and a geometric rearrangement of a five-co-ordinate intermediate before reco-ordination of the phosphine. The presence of free tertiary phosphine slightly reduces the rate of the isomerisation. For *mer*-$[IrCl_3(PEt_2Ph)_3]$ (3×10^{-3} mol dm^{-3} in $CHCl_3$), the addition of PEt_2Ph (9×10^{-3} mol dm^{-3}) leads to approximately 15% reduction in rate.[2] However, the addition of reagents such as bromoethane or allyl chloride that would quaternise PEt_2Ph does not affect the course of the isomerisation, indicating that extremely low concentrations of PEt_2Ph are present during the isomerisation if this is the mechanism.

In this paper we describe the isomerisation of the related complex *trans,mer*-$[IrCl_2(CN)(PEt_2Ph)_3]$ into the *fac* and the *cis,mer* isomers on irradiation with white light and show that both isomers are produced together in the early stages of the reaction, but that extended irradiation leads exclusively to the *cis,mer* isomer and not the *fac* as in the case of the trichloride complex. In the absence of an excess of chloride ion, μ-CN species are also observed as intermediates when the *fac* isomer is present, but these also disappear on extended irradiation as the *fac* isomer is converted into the *cis,mer* isomer.



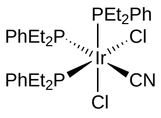
trans, mer

(A)



cis, mer

(B)



fac

(C)

Results and Discussion

Synthesis and characterisation of *trans,mer*-$[IrCl_2(CN)(PEt_2Ph)_3]$

We have shown that *trans,mer* complexes formed by substitution of the Cl ligand *trans* to PEt_2Ph in *mer*-$[IrCl_3(PEt_2Ph)_3]$ by anions are sensitive to irradiation with white light, leading to both alternative isomers. In the case of $[IrCl_2(CN)(PEt_2Ph)_3]$ three isomers are possible: *trans,mer* (**A**), *cis,mer* (**B**), and *fac* (**C**). Treatment of *mer*-$[IrCl_3(PEt_2Ph)_3]$ with NaCN (1 mol per mol iridium complex) in refluxing methanol gave 72% yield exclusively of one isomer which we have shown to be *trans,mer*-$[IrCl_2(CN)(PEt_2Ph)_3]$, closely related to the known PMe_2Ph complex.[4] The same isomer is formed when *trans,mer*-$[IrCl_2(H_2O)(PEt_2Ph)_3][ClO_4]$ is treated with cyanide ion.[4] The complex *trans,mer*-$[IrCl_2(CN)(PEt_2Ph)_3]$ **A** is easily characterised spectroscopically. Infrared bands for ν(CN) at 2127 cm^{-1} and for ν(IrCl) at 317 cm^{-1} (characteristic of chloride *trans* to chloride) are observed. The ^{31}P-{^1H} NMR spectrum shows the characteristic doublet (δ −31.0, $J_{PP} = 20.8$ Hz, mutually *trans* PEt_2Ph) and triplet (δ 42.84, $J_{PP} = 20.8$ Hz, unique PEt_2Ph) expected for a *mer* configuration. We also prepared *trans,mer*-$[IrCl_2(^{13}CN)(PEt_2Ph)_3]$ from the *mer*-trichloride and 90%-enriched $K^{13}CN$. This shows a strong ν(^{13}CN) band at 2080 cm^{-1} and a weak ν(^{12}CN) band at 2127 cm^{-1} in the expected intensity ratio. The ^{13}C-{^1H} NMR spectrum shows a double triplet for the ^{13}CN ligand [δ 111.0, J_{CP} (*trans*) = 115.7, J_{CP}(*cis*) = 14.0 Hz] which is only consistent with the *trans,mer* configuration. Carbon-13

Table 1 Bond lengths (Å) and angles (°) for the compound *trans,mer*-$[IrCl_2(CN)(PEt_2Ph)_3]$

Ir–P(1)	2.3992(13)	Ir–Cl(2)	2.3795(11)
Ir–P(2)	2.3849(10)	Ir–C(100)	2.025(5)
Ir–P(3)	2.3744(13)	C(100)–N(100)	1.139(6)
Ir–Cl(1)	2.3838(11)		
P(1)–Ir–P(2)	93.72(4)	P(3)–Ir–Cl(2)	86.68(4)
P(1)–Ir–P(3)	168.46(4)	Cl(1)–Ir–Cl(2)	176.29(4)
P(2)–Ir–P(3)	95.28(4)	P(1)–Ir–C(100)	85.8(2)
P(1)–Ir–Cl(1)	93.55(4)	P(2)–Ir–C(100)	175.42(14)
P(2)–Ir–Cl(1)	87.97(4)	P(3)–Ir–C(100)	85.8(2)
P(3)–Ir–Cl(1)	93.98(4)	Cl(1)–Ir–C(100)	87.51(14)
P(1)–Ir–Cl(2)	85.25(4)	Cl(2)–Ir–C(100)	88.89(14)
P(2)–Ir–Cl(2)	95.61(4)	Ir–C(100)–N(100)	177.5(5)

Table 2 Infrared and $^{13}C-\{^1H\}$ NMR data for the cyano ligands in *trans,mer* (**A**), *cis,mer* (**B**) and *fac* (**C**) isomers of $[IrCl_2(CN)(PEt_2Ph)_3]$ and in the μ-cyano species (**D**), *fac,fac*-$[(PhEt_2P)_3Cl_2Ir(\mu\text{-}CN)IrCl(CN)(PEt_2Ph)_3]Cl$

		$^{13}C-\{^1H\}$ NMR		
Complex	$\tilde{\nu}(CN)/cm^{-1}$	δ	$J_{PC}(cis)$/Hz	$J_{PC}(trans)$/Hz
A (*trans,mer*)	2127	111.0	14.0	115.7
B (*cis,mer*)	2116	99.4	9.5	
C (*fac*)	2133	109.4	11.5	121.0
D (*fac,fac*-μ-CN)				
μ-CN	2163	117.9	11.0	125.0
terminal CN	2133	108.3	11.0	119.0

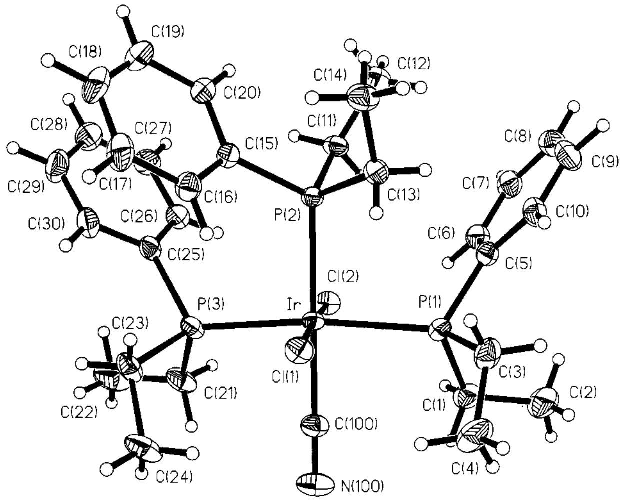


Fig. 1 Molecular structure of *trans,mer*-$[IrCl_2(CN)(PEt_2Ph)_3]$; ORTEP[5] plot with 30% thermal ellipsoids

enrichment was carried out so that we could use $^{31}C-\{^1H\}$ NMR spectra to detect the different isomers during isomerisations induced by irradiation.

The single-crystal structure of *trans,mer*-$[IrCl_2(CN)(PEt_2Ph)_3]$ was determined; the molecular structure is shown in Fig. 1 while selected bond lengths and angles are given in Table 1. The structure is as expected and confirms the configuration determined spectroscopically. A comparison with the structure of the *cis,mer* isomer is given below. Infrared and $^{13}C-\{^1H\}$ NMR data are given in Table 2.

Visible irradiation of *trans,mer*-$[IrCl_2(CN)(PEt_2Ph)_3]$

Solutions of the complex in dichloromethane (0.020 g in 5 cm^3) in sealed glass tubes were irradiated by a fluorescent lamp and the Fourier-transform IR spectra recorded at intervals in the ν(CN) region, 2200–2060 cm^{-1}. Fig. 2 shows the changes occurring in the spectra. In addition to the single absorption at 2127 cm^{-1} for the starting *trans,mer* isomer, there appear on irradiation three new bands at 2163, 2133 and 2116 cm^{-1} which grow in intensity at the expense of the original absorption. Eventually the original band is lost and the 2116 cm^{-1} band grows as the other bands at 2163 and 2133 cm^{-1} weaken and eventually disappear. After 17 h of irradiation only the band at 2116 cm^{-1} remains apart from a weak broad feature at 2144 cm^{-1} which remains unassigned.

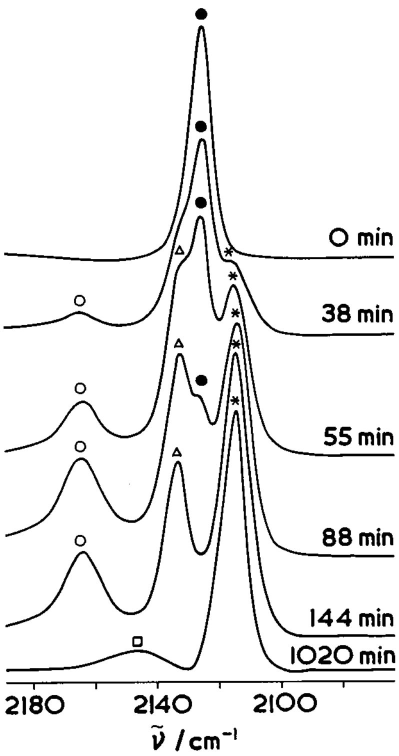


Fig. 2 Infrared spectra in the ν(CN) region for *trans,mer*-$[IrCl_2(CN)(PEt_2Ph)_3]$ in dichloromethane and after different times of visible irradiation

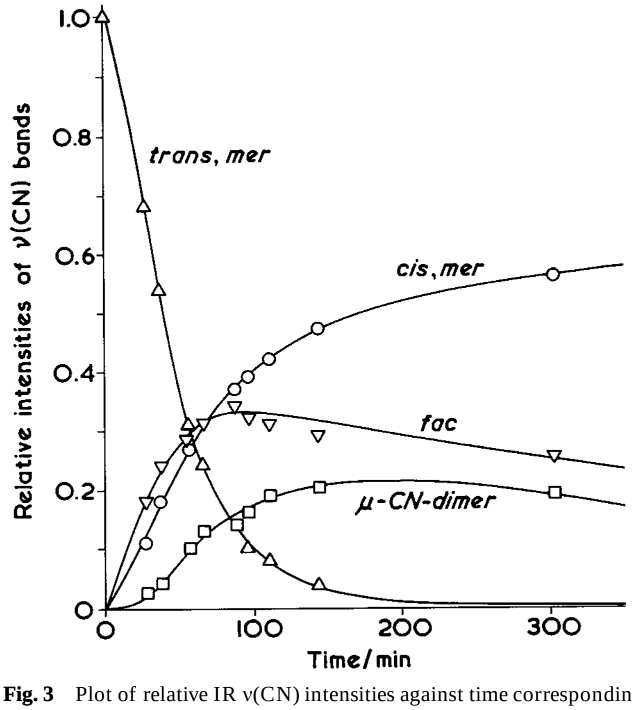


Fig. 3 Plot of relative IR ν(CN) intensities against time corresponding to changes of concentration of the *trans,mer*, *cis,mer* and *fac* isomers of $[IrCl_2(CN)(PEt_2Ph)_2]$ and of *fac,fac*-$[(PhEt_2P)_3Cl_2Ir(\mu\text{-}CN)IrCl(CN)(PEt_2Ph)_3]Cl$

Fig. 3 shows the variation of relative intensities of these four bands up to 6 h of irradiation and clearly four different cyano

Table 3 Bond lengths (Å) and angles (°) for the compound *cis,mer*-$[IrCl_2(CN)(PEt_2Ph)_3]$

Ir–P(1)	2.384(2)	Ir–Cl(2)	2.458(2)
Ir–P(2)	2.308(2)	Ir–C(100)	1.914(8)
Ir–P(3)	2.405(2)	Ir–Cl(2A)	2.460(11)[a]
Ir–Cl(1)	2.445(2)	N(100)–C(100)	1.135(2)[b]
P(1)–Ir–P(2)	95.88(7)	P(1)–Ir–C(100)	94.0(3)
P(1)–Ir–P(3)	168.25(7)	P(2)–Ir–C(100)	88.4(3)
P(2)–Ir–P(3)	93.66(7)	P(3)–Ir–C(100)	93.2(3)
P(1)–Ir–Cl(1)	85.11(7)	Cl(1)–Ir–C(100)	86.4(3)
P(2)–Ir–Cl(1)	174.76(7)	Cl(2)–Ir–C(100)	174.6(3)
P(3)–Ir–Cl(1)	86.02(7)	P(1)–Ir–Cl(2A)	93.0(3)
P(1)–Ir–Cl(2)	86.39(1)	P(2)–Ir–Cl(2A)	87.6(3)
P(2)–Ir–Cl(2)	96.86(8)	P(3)–Ir–Cl(2A)	94.2(3)
P(3)–Ir–Cl(2)	85.66(8)	Cl(1)–Ir–Cl(2A)	87.2(3)
Cl(1)–Ir–Cl(2)	88.33(8)	Cl(2)–Ir–Cl(2A)	175.5(3)
C(100)–Ir–Cl(2A)[c]	1.3(5)	Ir–C(100)–N(100)	176.7(9)

[a] Cl(2A) in the minor disordered form with refined population of 0.204(5). The atom overlies C(100)N(100). [b] Contrained to be this value. [c] Cl(2A) and C(100)N(100) are overlapping.

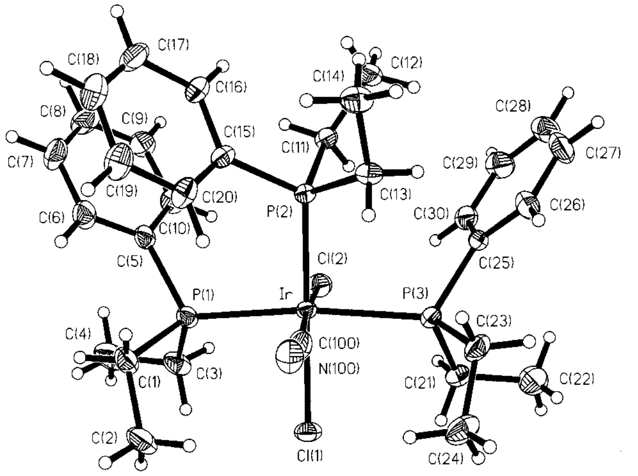


Fig. 4 Molecular structure of *cis,mer*-$[IrCl_2(CN)(PEt_2Ph)_3]$; ORTEP[5] plot with 30% thermal ellipsoids

species are present for much of this period. The original *trans,-mer* isomer has essentially disappeared after 3 h and after 17 h one isomer only remains. We originally expected this to be the *fac* isomer (**C**) in the light of the isomerisation of *mer*-$[IrCl_3(PEt_2Ph)_3]$ to its *fac* isomer but we have shown that the final product is actually the *cis,mer* isomer (**B**). The ^{13}C-{^1H} NMR spectrum of the ^{13}C-enriched final product $[IrCl_2(^{13}CN)(PEt_2Ph)_3]$ is a 1:3:3:1 quartet at δ 99.4 ($J_{PC} = 9.5$ Hz) showing that all three PEt_2Ph ligands are *cis* to the ^{13}CN ligand and with indistinguishable J_{PC} values, which is consistent with the *cis,mer* isomer. Isolation of the final product as crystals allowed the single-crystal structure to be determined which is shown in Fig. 4. Selected bonds lengths and angles are given in Table 3. Hence there can be no doubt that the final product after extended visible irradiation is the *cis,mer* isomer. This isomer has ν(CN) at 2116 cm^{-1} and the intermediates have ν(CN) at 2133 and 2163 cm^{-1}.

To identify these intermediates we followed the course of the photolysis by ^{13}C-{^1H} NMR spectra for the ^{13}CN-enriched species *trans,mer*-$[IrCl_2(^{13}CN)(PEt_2Ph)_3]$. In the early stages after 12 min of irradiation (Fig. 5) two new signals are apparent: a 1:3:3:1 quartet at δ 99.4 ($J_{PC} = 9.5$ Hz) for the *cis,mer* isomer (as already described above) and a new double triplet at δ 109.4 ($J_{cis} = 11.5$, $J_{trans} = 121.0$ Hz) for the *fac* isomer. Therefore both other isomers appear at the early stages of the reaction; after 12 min of irradiation the isomeric composition is *trans,mer* 0.79, *fac* 0.12, *cis,mer* 0.09. The plots of ν(CN) intensities (Fig. 3) show that the two new isomers are produced initially, both almost certainly as direct photoproducts from the *trans,mer* isomer.

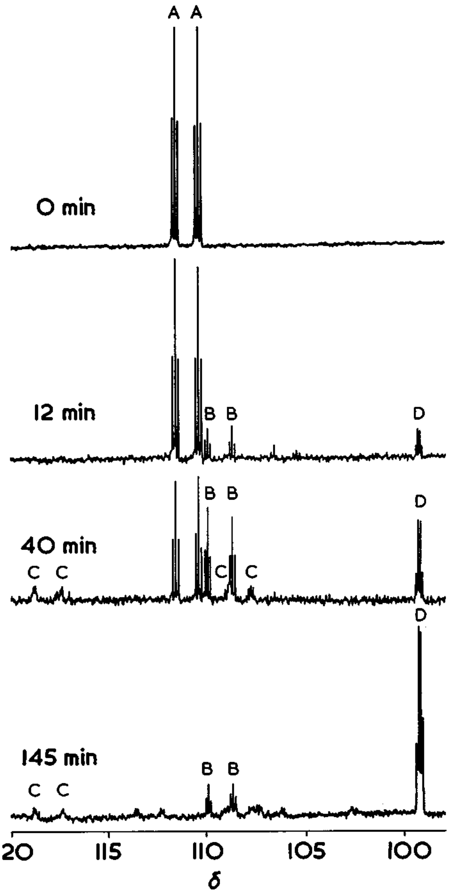


Fig. 5 The ^{13}C-{^1H} NMR spectra of *trans,mer*-$[IrCl_2(^{13}CN)(PEt_2Ph)_3]$ in CH_2Cl_2 and after periods of visible irradiation

As photolysis continues both *fac* and *cis,mer* isomers increase in concentration and then additional ^{13}C-{^1H} NMR signals at δ 117.9 (ddt, μ-CN) and 108.3 (dt, terminal CN) appear for a secondary product which we assign to the μ-CN species $[(PhEt_2P)_3Cl_2Ir(\mu\text{-}CN)IrCl(CN)(PEt_2Ph)_3]Cl$ which has ν(CN) at 2163 (μ-CN) and 2133 cm^{-1} (terminal CN). We reported earlier that the μ-CN species $[(PhMe_2P)_3Cl_2Ir(\mu\text{-}CN)IrCl_2(PMe_2Ph)_3][ClO_4]$ can be synthesized by treatment of *trans,mer*-$[IrCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ with *trans,mer*-$[IrCl_2(CN)(PMe_2Ph)_3]$.[4] This μ-CN species with PMe_2Ph ligands was fully characterised by ^1H, ^{13}C-{^1H}, ^{15}N and ^{31}P-{^1H} NMR, IR spectra and single-crystal structure determination. The μ-CN ligand in this complex is of the normal linear M–CN–M type and is characterised by ν($^{12}C^{14}N$) at 2159 cm^{-1} (compare with 2163 cm^{-1} for the reaction intermediate in the photolysis reaction described above). A ^{13}C-{^1H} NMR signal at δ 118.5 for $[(PhMe_2P)_3Cl_2Ir(\mu\text{-}CN)IrCl_2(PMe_2Ph)_3][ClO_4]$ can be compared with δ 117.9 for the photoreaction intermediate. Higher ν(CN) and ^{13}C-{^1H} NMR δ values are associated with μ-CN compared with terminal CN. The starting *trans,mer* species in solution is pure prior to irradiation and shows no tendency to dimerise in this way with chloride displacement. The reason for this is that the *trans,mer* isomer has no labile Cl (the two Cl ligands are mutually *trans*) whereas the *fac* and *cis,mer* isomers have Cl *trans* to PEt_2Ph which are expected to be easily displaced by an incoming cyano-complex. For this reason there is a small induction period for the formation of the μ-CN complex as the concentrations of other isomers increase; see Fig. 3.

A key experiment in respect of this μ-CN species was the irradiation of *trans,mer*-$[IrCl_2(CN)(PEt_2Ph)_3]$ in the presence of an excess of $[N(PPh_3)_2]Cl$ in dichloromethane. The isomerisation of *trans,mer* to *fac* and *cis,mer* isomers occurs unperturbed except for a slightly higher rate (not measured

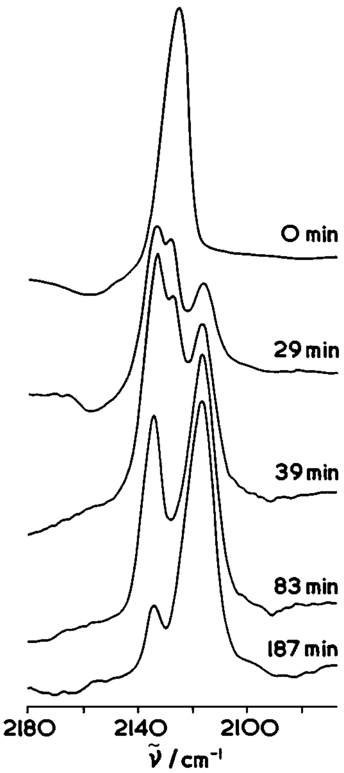
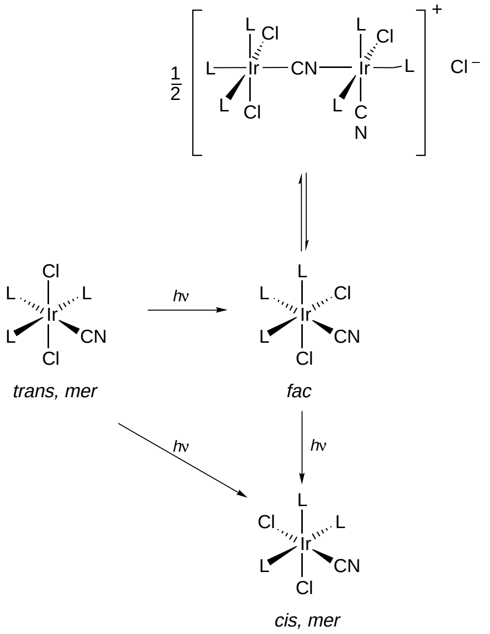
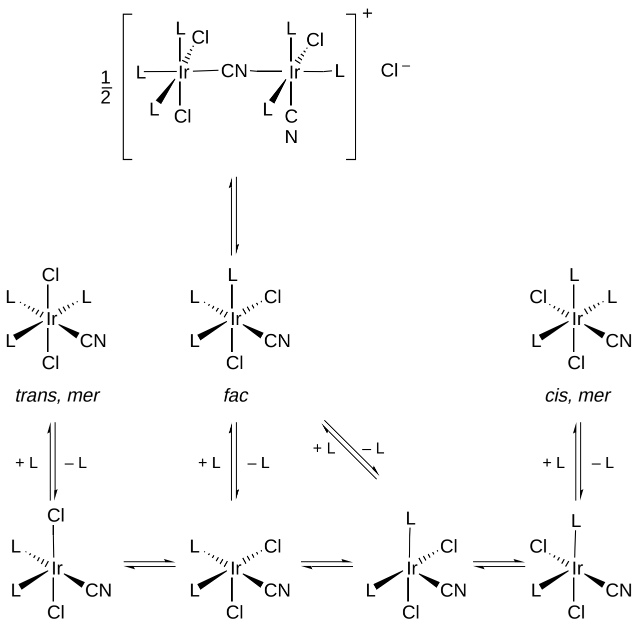


Fig. 6 Infrared spectra in the ν(CN) region for *trans,mer*-$[IrCl_2(CN)(PEt_2Ph)_3]$ in chloromethane with a large excess of $[N(PPh_3)_2]Cl$ and after different times of visible irradiation



Scheme 1 L = PEt_2Ph

quantitatively). This supports the idea that PEt_2Ph rather than Cl^- dissociation is the main mechanism for isomerisation (see below). However, there was no evidence for the formation of the μ-CN species in the presence of free chloride ion which is totally consistent with the proposed formation of the μ-CN species by chloride displacement (Fig. 6). The course of the reaction we propose is shown in Scheme 1. When the reaction was photolysed for a period and the mixture kept in the dark no further change occurred so that all isomerisations appear to be photoinduced and are not reversed thermally at room temperature. The μ-CN species is derived from the *fac* isomer since it is not present at the beginning of the reaction (only *trans,mer* present), nor at the end of the reaction (only *cis,mer* present),



Scheme 2 L = PEt_2Ph

nor in the presence of an excess of chloride ion. We therefore propose that the μ-CN species is *fac,fac*-$[(PhEt_2P)_3Cl_2Ir(\mu\text{-}CN)IrCl(CN)(PEt_2Ph)_3]Cl$. The salt could not be isolated even on addition of suitable large anions to induce crystallisation. The problem is that it was never obtained as more than a minor component in a mixture with other complexes.

Attempting to isolate the *fac* isomer of $[IrCl_2(CN)(PEt_2Ph)_3]$ to complete the crystal structures of all three possible isomers, we irradiated a more concentrated solution of the *trans,mer* isomer for 165 min until all three isomers were in significant concentration (by IR estimation). Thin-layer chromatography on SiO_2 in the dark eluting with chloromethane gave one pale yellow and two colourless bands. However, extraction of these bands and checking their IR spectra showed them to be mixtures: μ-CN species plus *cis,mer*, *fac* plus *cis,mer*, and *trans,mer* plus *cis,mer* isomers respectively. The *fac* isomer was found to be inseparable from the *cis,mer* isomer and therefore we have only been able to characterise it spectroscopically.

The mechanism as discussed earlier for the *mer* to *fac* isomerisation of $[IrCl_3(PEt_2Ph)_3]$ probably involves PEt_2Ph dissociation, although the presence of reagents such as allyl chloride or bromoethane, which are expected to quaternise PEt_2Ph, do not interfere with the formation of the *fac* isomer.[2] However, photolysis does lead to phosphine exchange which does not occur in the absence of light and this is consistent with phosphine dissociation. Scheme 2 shows a similar mechanism for *trans,mer*-$[IrCl_2(CN)(PEt_2Ph)_3]$. The five-co-ordinate short-lived intermediates are expected to be square-pyramidal and stereochemically non-rigid leading to various isomeric five-co-ordinate species which on reco-ordination of the PEt_2Ph give the *fac* and *cis,mer* isomers of $[IrCl_2(CN)(PEt_2Ph)_3]$. Following the photoisomerisation by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy gave no evidence for free PEt_2Ph, so its concentration must be very low if this mechanism is correct. Alternative intramolecular mechanisms, such as Bailar or Ray-Dutt twists,[6] could be considered but these would not account for the photochemically induced phosphine exchange. Other examples of photochemically induced isomerisations of d^6-rhodium or -iridium complexes are believed to occur dissociatively, for example the isomerisation of *mer,cis*-$[RhCl_3(Me_2SO\text{-}O)(Me_2SO\text{-}S)_2]$ to the *mer,trans* isomer.[7]

Crystal structures of *trans,mer*-and *cis,mer*-$[IrCl_2(CN)(PEt_2Ph)_3]$

The crystal structures of these isomers (Figs. 1 and 4) are consistent with spectroscopic data. The crystals of the *trans*,*mer* and *cis*,*mer* isomers are almost isomorphous, the structures being controlled largely by the *mer*-$\mathrm{Ir(PEt_2Ph)_3}$ set of atoms which are almost identical. The structure of the *cis*,*mer* isomer was complicated by some disorder between the arrangement shown in Fig. 4 and another with the cyanide C(100)N(100) and Cl(2) with reversed positions. The populations of these two arrangements were refined and the most abundant arrangement is that shown in Fig. 4 with a population of 0.796(5). The two *mer* isomers were completely pure isomerically and the disorder is not the result of an isomeric mixture. However, in view of the almost isomorphous nature of these crystals we would have expected an isomeric mixture to cocrystallise. This is not the case here. Owing to the disorder in the *cis*,*mer* isomer, it was difficult to obtain an accurate geometry for the cyanide ligand with population 0.796(5) because it overlays a Cl of the minor form with population 0.204(5). To allow the refinement of a chemically reasonable structure, the C(100)−N(100) distance was constrained to be 1.135 Å. Other details of the structure, such as the Ir−P and Ir−Cl distances, are probably reliable and the thermal parameters for these atoms are well behaved.

Having these structures allows some comparisons to be made between the *trans* influences of the Cl, CN and $\mathrm{PEt_2Ph}$ ligands. For example, Ir−Cl distances depend upon the ligand *trans* to Cl: 2.458(2) (Cl*trans* to CN), 2.443(2) (Cl*trans* to $\mathrm{PEt_2Ph}$) and 2.384(1), 2.379(1) Å (Cl*trans* to Cl). The *trans* influences are in the order CN > $\mathrm{PEt_2Ph}$ > Cl. The CN and $\mathrm{PEt_2Ph}$ ligands also have *trans* influences greater than that of Cl in comparing Ir−P distances but it is not possible to separate CN from $\mathrm{PEt_2Ph}$ in this case. Thus Ir−P distances are 2.310(2) ($\mathrm{PEt_2Ph}$ *trans* to Cl), 2.386(1) ($\mathrm{PEt_2Ph}$ *trans* to CN) and 2.400(1), 2.374(1), 2.407(2) and 2.384(2) Å ($\mathrm{PEt_2Ph}$ *trans* to $\mathrm{PEt_2Ph}$). However, there are significant differences in the Ir−P distances for the two mutually *trans* $\mathrm{PEt_2Ph}$ ligands in both *mer* complexes so that *trans* influences are not the only controlling factors. We believe that the conformations of the $\mathrm{PEt_2Ph}$ ligands are also significant. Each $\mathrm{PEt_2Ph}$ ligand has two substituents above and one below the $\mathrm{IrP_3}$ plane. The mutually *trans* $\mathrm{PEt_2Ph}$ ligands are eclipsed while the unique $\mathrm{PEt_2Ph}$ ligand adopts a less symmetrical conformation which is favoured because it allows a close parallel alignment of the two Ph substituents (see Figs. 1 and 4). This parallel alignment is associated with shorter Ir−P bond lengths. Thus for the mutually *trans* $\mathrm{PEt_2Ph}$ ligands in these complexes the Ir−P distances are 2.374(1) and 2.384(2) Å for the Ph-aligned phosphines and significantly longer for the others, 2.400(1) and 2.407(2) Å. We have described earlier how, when iridium complexes are heavily stacked with tertiary phosphines, these parallel phenyl alignments have a major effect on the structures and that barriers to rotation about M−P bonds can be large enough to lead to slow exchange and to separate ^{31}P NMR signals for the different rotamers.[8,9] The complex *trans*-$\mathrm{[IrCl_2(PMe_2Ph)_4]^+}$ exists as three non-interconverting rotamers at low temperatures.[8] In the case of *tris*-diethylphenylphosphine *mer* complexes, crowding is insufficient to prevent rapid exchange of the *trans* $\mathrm{PEt_2Ph}$ ligands by rotation about Ir−P bonds in solution, but sufficient to influence Ir−P bond lengths.

Conclusion

Whereas yellow *mer*-$\mathrm{[IrCl_3(PEt_2Ph)_3]}$ photoisomerises to the *fac* isomer which is extremely insoluble and forms colourless crystals, *trans*,*mer*-$\mathrm{[IrCl_2(CN)(PEt_2Ph)_3]}$ gives the *fac* and the *cis*,*mer* isomers photochemically. All isomers remain in solution so the isomerisations can be followed straightforwardly and extended photolysis leads exclusively to the *cis*,*mer* isomer. Formation of the bridged cyanide dinuclear complex *fac*,*fac*-$\mathrm{[(PhEt_2P)_3Cl_2Ir(\mu\text{-}CN)IrCl(CN)(PEt_2Ph)_3]Cl}$ during the course of the isomerisation is suppressed by addition of chloride ion in the form of $\mathrm{[N(PPh_3)_2]Cl}$, but this does not alter the course of the isomerisation of *trans*,*mer*-$\mathrm{[IrCl_2(CN)(PEt_2Ph)_3]}$ to the *fac* and the *cis*,*mer* isomers.

Table 4 Crystal data and structure solution and refinement parameters for the compounds *trans*,*mer*- and *cis*,*mer*-$\mathrm{[IrCl_2(CN)(PEt_2Ph)_3]}$[a]

	trans,*mer*	*cis*,*mer*
Crystal size/mm	0.17 × 0.40 × 0.45	0.18 × 0.18 × 0.28
a/Å	10.719(2)	10.555(2)
b/Å	13.994(1)	13.783(2)
c/Å	22.437(4)	22.838(5)
β/°	92.50(2)	93.58(2)
U/Å^3	3362.4(9)	3316(1)
D_c/g cm^{-3}	1.56	1.58
μ(Mo-Kα)/cm^{-1}	42.78	43.38
No. orientation reflections, 2θ range/°	32, 17–29	30, 13–27
2θ Range/°	5–53	5–50
hkl Range	0,0,−29 to 14,18,29	0,0,−28 to 3,17,28
Total data	7622	6362
Unique data	6935	5761
Parameters in refinement	343	336
R (all data)[b]	0.0413	0.0562
[$I > 2\sigma(I)$][b]	0.0313	0.0417
$wR2$ (all data)[c]	0.0915	0.1100
Goodness of fit	1.014	1.089
Maximum Δ/σ	0.001	0.001
Maximum peak, hole in final difference Fourier map/e Å^{-3}	1.33, −1.00	1.75, −1.11

[a] Common to both compounds: colourless crystals, formula = $\mathrm{C_{31}H_{45}Cl_2IrNP_3}$, $M = 787.78$, monoclinic, space group, $P2_1/n$, $Z = 4$, $F(000) = 1576$, ω scan mode, direct methods structure solution. Graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å), three standard reflections every 97, no decay, data corrected for absorption empirically by ψ-scan method, maximum and minimum transmission 1.000 and 0.352 for *trans*,*mer* and 0.920 and 0.545 for *cis*,*mer*, full-matrix least-squares refinement of F^2. [b] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [c] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$ for all data.

Experimental

Materials

Chloroiridic acid, diethylphenylphosphine and K^{13}CN were used as purchased from Aldrich. The 400 MHz NMR spectra were obtained on a Varian VXR400 spectrometer and IR spectra on a Nicolet 280 FTIR spectrometer. The complex *mer*-$\mathrm{[IrCl_3(PEt_2Ph)_3]}$ was prepared as yellow crystals in 79% yield from chloroiridic acid and $\mathrm{PEt_2Ph}$ in refluxing ethanol and HCl following a reported method.[1]

Synthesis of *trans*,*mer*-$\mathrm{[IrCl_2(CN)(PEt_2Ph)_3]}$

The complex *mer*-$\mathrm{[IrCl_3(PEt_2Ph)_3]}$ (0.200 g) and sodium cyanide (0.0248 g) were dissolved in methanol (20 cm^3) and the solution refluxed for 2 h. The solution was filtered and the volume reduced on a Rotavap down to 15 cm^3. Bright yellow crystals (0.142 g, 72%) deposited overnight at room temperature (Found: C, 47.1; H, 5.6; Cl, 9.1; N, 1.85. $\mathrm{C_{31}H_{45}Cl_2IrNP_3}$ requires C, 47.25; H, 5.75; Cl, 9.0; N, 1.8%). The complex *trans*,*mer*-$\mathrm{[IrCl_2(^{13}CN)(PEt_2Ph)_3]}$ was prepared similarly using 90%-enriched K^{13}CN.

Photolysis reactions

Reactions were carried out by photolysing dichloromethane solutions in Pyrex tubes placed next to a fluorescent tube. They were not carried out quantitatively in terms of light intensities but care was taken to keep the light intensity constant in a given experiment. When monitoring by IR spectroscopy, samples were removed by syringe and IR spectra recorded in 0.1 cm thickness cell with $\mathrm{CaF_2}$ windows. Reactions were carried out in

NMR tubes when the reaction was being monitored by ^{13}C NMR spectroscopy.

Crystallography

Colourless crystals of both isomers were grown from methanol–dichloromethane mixtures. X-Ray data were collected at 20 °C using a Nicolet R3v/m diffractometer with crystals mounted in air. Details of the crystal structure determinations are given in Table 4. Structures were solved by direct methods using SHELXTL PLUS[10] and refined using SHELXL 93.[11] All non-H atoms of the *trans*,*mer* isomer were refined anisotropically. Disorder of the mutually *trans* CN and Cl ligands in the *cis*,*mer* isomer made it necessary that the cyanide group, C(100)N(100), of the major form with a refined population of 0.796(5) and the chloride, Cl(2A), of the minor form with a population of 0.204(5) be refined isotropically with the C(100)–N(100) distance constrained to be 1.135 Å. All other non-H atoms were refined anisotropically. The CN group of the minor form was not included in the model. Hydrogen atoms in both crystals were included in idealised positions, riding upon their respective carbon atoms, with C–H distances fixed at 0.96 Å and isotropic thermal parameters at 0.08 $Å^3$.

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