

PREPARATION AND REACTIVITY OF *trans*-Ir(CH₂CN)(CO)(PPh₃)₂

SANDRO ZECCHIN, GIANNI ZOTTI and GIUSEPPE PILLONI

*Consiglio Nazionale delle Ricerche, Istituto di Polarografia ed Elettrochimica Preparativa,
Corso Stati Uniti 4, 35100 Padova (Italy)*

(Received April 1st, 1982)

Summary

The preparation and characterization of the complex *trans*-Ir(σ -CH₂CN)(CO)(PPh₃)₂ are described. Like the isoelectronic and isostructural Vaska's complex, this iridium(I) derivative undergoes reactions with many simple molecules (CO, O₂, HClO₄, CH₃I and H₂) and is the precursor of a variety of novel iridium compounds whose stereochemistry has been assigned by IR and ¹H NMR spectroscopy. Notably, the reaction with CH₃I affords an unusually stable iridium(III) complex containing two metal–carbon σ bonds, while the *cis*-addition of hydrogen appears to follow a stereochemical pathway leading uniquely to the formation of a rare dihydrido derivative having the phosphine ligands *cis* to each other and *trans* to H.

Introduction

During our current electrochemical investigations on mixed carbonyltriphenylphosphineiridium(I) complexes in acetonitrile [1] we obtained a stable species which was identified as the previously unreported cyanomethyl complex of iridium(I), *trans*-Ir(CH₂CN)(CO)(PPh₃)₂. Cyanomethyl complexes of transition metals in low oxidation state are not uncommon, and among the more extensively investigated are the derivatives of *d*⁸ metals palladium(II) and platinum(II) [2]. As far as iridium(I) is concerned, only tricyano- and dicyano-methyl derivatives have been so far reported and all of them are believed to be keteniminato complexes, i.e. to contain the Ir–N=C=C' linkage [3–5]. Also, in spite of the interest in analogues of Vaska's complex, *trans*-IrCl(CO)(PPh₃)₂ [6], only a few stable organometallic derivatives of these iridium(I) complexes are known [7–14].

This paper deals with the preparation and characterization of *trans*-Ir(CH₂CN)(CO)(PPh₃)₂. The reactions of the novel complex with some electrophilic reagents (CO, O₂, HClO₄, CH₃I and H₂) and the spectroscopic properties of the products are reported.

Results and discussion

Preparation and characterization of trans-Ir(CH₂CN)(CO)(PPh₃)₂ (I)

The electrochemical procedure we had already found to be very suitable for obtaining d^8 rhodium and iridium organometallic derivatives [14] was successfully applied to the preparation of the title compound. Thus, the two-electron reduction of the parent d^6 species, $\text{IrCl}(\text{CH}_2\text{CN})(\text{CO})(\text{PPh}_3)_2$, (see Experimental section) in acetonitrile affords in high yield complex I as lemon-yellow bright crystals which separate during the electrolysis.

Complex I is insoluble in aliphatic hydrocarbons and alcohols, moderately soluble in acetonitrile but very soluble in chloroalkanes and aromatic solvents. It is stable under inert atmospheres in solution and in the solid state, is diamagnetic, and behaves as non-electrolyte. Analytical data are listed in Table 1. The formulation *trans*- $\text{Ir}(\sigma\text{-CH}_2\text{CN})(\text{CO})(\text{PPh}_3)_2$ was confirmed by IR and ^1H NMR spectroscopy. The data are summarized in Tables 1 and 2.

The infrared spectrum of I exhibits, in addition to absorption bands due to the phosphine ligands, a medium intensity band at 2202 cm^{-1} and a strong absorption at 1957 cm^{-1} assigned to $\nu(\text{C}\equiv\text{N})$ and $\nu(\text{CO})$, respectively; the presence of the methylene group is revealed by weak signals at 2930 and 2900 cm^{-1} . In contrast to the above mentioned cyanomethyl complexes of iridium(I) [3–5], no absorption band corresponding to the $\nu(\text{N}=\text{C}=\text{C})$ frequencies expected for a possible formulation of I as keteniminato complex is observed.

The position of the carbonyl band relative to that of the closely related complex, *trans*- $\text{Ir}(\text{CH}_3)(\text{CO})(\text{PPh}_3)_2$ (1935 cm^{-1}) [12], suggests a decrease in metal electron density consistent with the presence of the electron-withdrawing cyano group on the methylenic ligand.

The electronic spectrum of I is very similar to those of the structurally well established *trans*- $\text{IrX}(\text{CO})\text{P}_2$ [15], showing maxima at 350, 405 and 472 nm with molar extinction coefficients of 3400, 3600, and $700\text{ M}^{-1}\text{ cm}^{-1}$, respectively (CH_3CN soln).

Finally, the mutual *trans* disposition of the two triphenylphosphines is inferred from the ^1H NMR spectrum, the cyanomethyl protons appearing as a well-defined 1/2/1 triplet resonance at τ 9.33 ($J(\text{PH})$ 9 Hz) with the expected 15/1 integrated intensity ratio of phenyl- to methylene protons.

Like the isoelectronic and isostructural Vaska's complex, compound I undergoes reactions with many simple molecules and it is the precursor of a variety of novel iridium derivatives. The reactions we have studied are depicted in Fig. 1; pertinent analytical and spectroscopic data of the products are collected in Tables 1 and 2.

Reaction with carbon monoxide

Yellow solutions of I are immediately decolourized by carbon monoxide at 1 atm at 25°C producing $\text{Ir}(\text{CH}_2\text{CN})(\text{CO})_2(\text{PPh}_3)_2$ (II) and the reaction can be completely reversed in a few minutes by simply passing a stream of nitrogen through the solution. No insertion of CO into the $\text{Ir}-\text{C}$ σ bond takes place even on prolonged treatment; the difficulty of bringing about insertion with cyano-alkyl complexes has been noted previously [16,17]. Under these conditions,

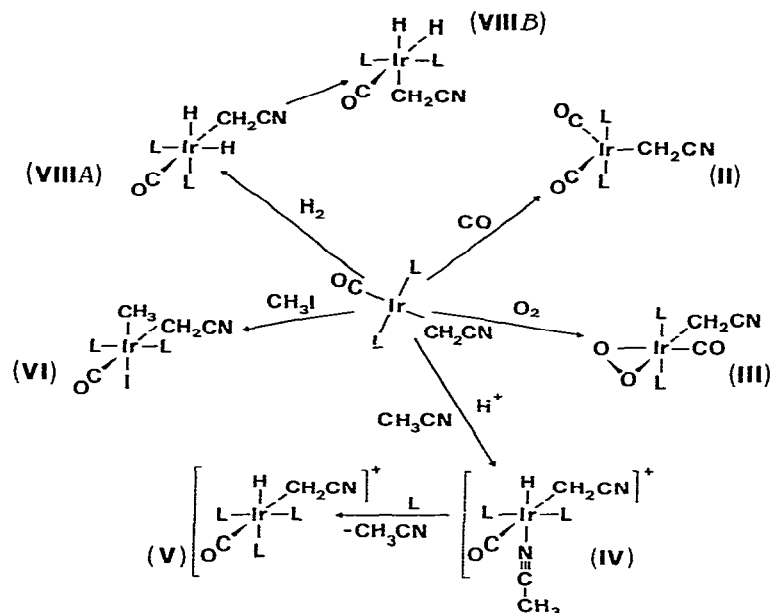


Fig. 1. Reactions of $\text{trans-Ir}(\text{CH}_2\text{CN})(\text{CO})\text{PPh}_3_2$.

however, some tricarbonylated species is also formed, unless a slight excess of triphenylphosphine is present.

The infrared spectrum of the recovered white solid shows, in addition to $\nu(\text{CN})$ at 2210 cm^{-1} , two terminal carbonyl stretching vibrations at 1970 and 1920 cm^{-1} consistent with a five-coordinate species having *cis* carbonyl groups. In solution each of these two carbonyl ligands gives rise to two bands; a typical spectrum, along with the spectrum of the solid for comparison, is shown in Fig. 2. The positions of the bands are similar in different solvents, but the intensities of the *A* bands relative to the *B* bands are strongly solvent dependent, the ratios decreasing as the polarity of the solvent is increased. Furthermore there is no significant change in the spectrum either in the presence of varying amounts of triphenylphosphine or at various temperatures in the range -20 to $+40^\circ\text{C}$. The same final IR profile is observed when the addition of CO to complex I is monitored in solution, and the white solids recovered from different solvents give identical spectra.

Related behaviour was reported for the dicarbonylated iridium complex, $\text{IrH}(\text{CO})_2(\text{PPh}_3)_2$ [18]. By analogy, the establishment in solution of a chemical equilibrium between two isomeric species, A and B, of $\text{Ir}(\text{CH}_2\text{CN})(\text{CO})_2(\text{PPh}_3)_2$ is thus strongly suggested. The average ratio between the intensities of the anti-symmetric and the symmetric $\nu(\text{CO})$ frequencies of species A is ~ 0.9 while it is 2.77 for species B. From the equation $I_{\text{antisym}}/I_{\text{sym}} = (1 - \cos \delta)/(1 + \cos \delta)$ [19] the OC-Ir-CO bond angle, δ , is found to be ~ 87 and 117° for A and B, respectively. On the assumption that the bond moments for all the CO groups are the same, it appears that B is more abundant than A. Since the $\text{A} \rightleftharpoons \text{B}$ equilibrium lies more to the left-hand side in apolar solvents than in the polar ones, formulation of A as a six-coordinate solvated species appears to be unlikely.

TABLE I
ANALYTICAL AND IR SPECTRAL ^a DATA

	Complex	m.p. (dec.) ^b (°C)	Analysis (Found (calcd.) (%))		$\nu(\text{CO})$ (cm ⁻¹)	$\nu(\text{CN})$ (cm ⁻¹)	others (cm ⁻¹)
I	$\text{Ir}(\text{CH}_2\text{CN})(\text{CO})(\text{PPh}_3)_2$	220—222	60.2 (59.68)	4.25 (4.11)	1957 (1960)	2202 (2194)	
II	$\text{Ir}(\text{CH}_2\text{CN})(\text{CO})_2(\text{PPh}_3)_2$	120—125	59.0 (59.10)	3.85 (3.97)	1970, 1920 (2024, 1984, 1952, 1932) ^c	2210 (2208)	
III	$\text{Ir}(\text{O}_2)(\text{CH}_2\text{CN})(\text{CO})(\text{PPh}_3)_2$	171—173	57.8 (57.34)	3.90 (3.95)	1989 (1994)	2218 (2209)	835, $\nu(\text{OO})$
IVA	$[\text{IrH}(\text{CH}_2\text{CN})(\text{CH}_3\text{CN})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$	165—167	53.3 (53.16)	3.88 (3.92)	2045 (2065)	2214 (2214)	2244, $\nu(\text{CH}_3\text{CN})$
IVB	$[\text{IrH}(\text{CH}_2\text{CN})(\text{CH}_3\text{CN})(\text{CO})(\text{PPh}_3)_2]\text{PF}_6$	172—174	50.4 (50.67)	3.70 (3.73)	2043 (2065)	2214 (2214)	2242, $\nu(\text{CH}_3\text{CN})$
VB	$[\text{IrH}(\text{CH}_2\text{CN})(\text{CO})(\text{PPh}_3)_3]\text{PF}_6$	115—117	56.4 (57.38)	3.91 (4.06)	2038 (2044)	2214 (2215)	
VI	$\text{Ir}(\text{CH}_2\text{CN})(\text{CH}_3)(\text{CO})(\text{PPh}_3)_2$	190—193	52.1 (51.84)	3.96 (3.81)	2009, 1995 ^{d,e} (2011)	2209 ^e (2206)	
VII	$\text{IrCl}(\text{CH}_2\text{CN})(\text{CH}_3)(\text{CO})(\text{PPh}_3)_2$	205—208	57.8 (57.46)	4.13 (4.19)	2030, 2010 ^{d,e} (2017)	2210 ^e (2207)	
VIII, isomer A	$\text{IrH}_2(\text{CH}_2\text{CN})(\text{CO})(\text{PPh}_3)_2$	130—135	59.2 (59.53)	4.40 (4.35)	2004 (2011)	2205 (2205)	2102 $\nu(\text{Ir-H})$ (2094)
VIII, isomer B	$\text{IrH}_2(\text{CH}_2\text{CN})(\text{CO})(\text{PPh}_3)_2$	160—165	59.6 (59.53)	4.36 (4.35)	1985 (1986)	2190 (2192)	2090 $\nu(\text{Ir-H})$ (2085)
IX, isomer A	$\text{IrD}_2(\text{CH}_2\text{CN})(\text{CO})(\text{PPh}_3)_2$	—	—	—	2005 (2011)	2205 (2205)	1505, $\nu(\text{Ir-D})$
IX, isomer B	$\text{IrD}_2(\text{CH}_2\text{CN})(\text{CO})(\text{PPh}_3)_2$	—	—	—	2014 (2018)	2190 (2191)	

^a Nujol mull (CH_2Cl_2 soln), ^b Under vacuum, uncorrected, ^c Solution isomers, ^d Solid state splitting, ^e In CsI disk.

TABLE 2
¹H NMR SPECTRAL DATA ^{a,b}

	Complex	$\tau(\text{CH}_2)$ (ppm)	$J(\text{PH})$ (Hz)	$\tau(\text{others})$ (ppm)	$J(\text{PH})$ (Hz)
I	$\text{Ir}(\text{CH}_2\text{CN})(\text{CO})(\text{PPh}_3)_2$	9.33t	9	—	—
II	$\text{Ir}(\text{CH}_2\text{CN})(\text{CO})_2(\text{PPh}_3)_2$	8.92 ^c	—	—	—
III	$\text{Ir}(\text{O}_2)(\text{CH}_2\text{CN})(\text{CO})(\text{PPh}_3)_2$	8.12t	5	—	—
IV	$[\text{IrH}(\text{CH}_2\text{CN})(\text{CH}_3\text{CN})(\text{CO})(\text{PPh}_3)_2]^+$	8.77t	9	27.47t (Ir—H)	12
V	$[\text{IrH}(\text{CH}_2\text{CN})(\text{CO})(\text{PPh}_3)_3]^+$	8.40q	—	8.03s (CH_3CN)	—
VI	$\text{IrI}(\text{CH}_2\text{CN})(\text{CH}_3)(\text{CO})(\text{PPh}_3)_2$	8.94t	8	21.44dt (Ir—H)	16(cis), 139(trans)
VII	$\text{IrCl}(\text{CH}_2\text{CN})(\text{CH}_3)(\text{CO})(\text{PPh}_3)_2$	8.53t	8.5	9.68t (Ir— CH_3)	5
VIII Isomer A	$\text{IrH}_2(\text{CH}_2\text{CN})(\text{CO})(\text{PPh}_3)_2$	9.53t	7	10.21t (Ir— CH_3)	5
VIII Isomer B	$\text{IrH}_2(\text{CH}_2\text{CN})(\text{CO})(\text{PPh}_3)_2$	9.35t	9	20.18m (Ir—H)	—
			5	19.92t (OC—Ir—H)	18
				22.34t (Ir—Ir— CH_2CN)	16

^a In CD_2Cl_2 at room temperature. TMS as internal standard. ^b d: doublet; t: triplet; q: quartet; s: singlet; m: multiplet. ^c Broad, see text.

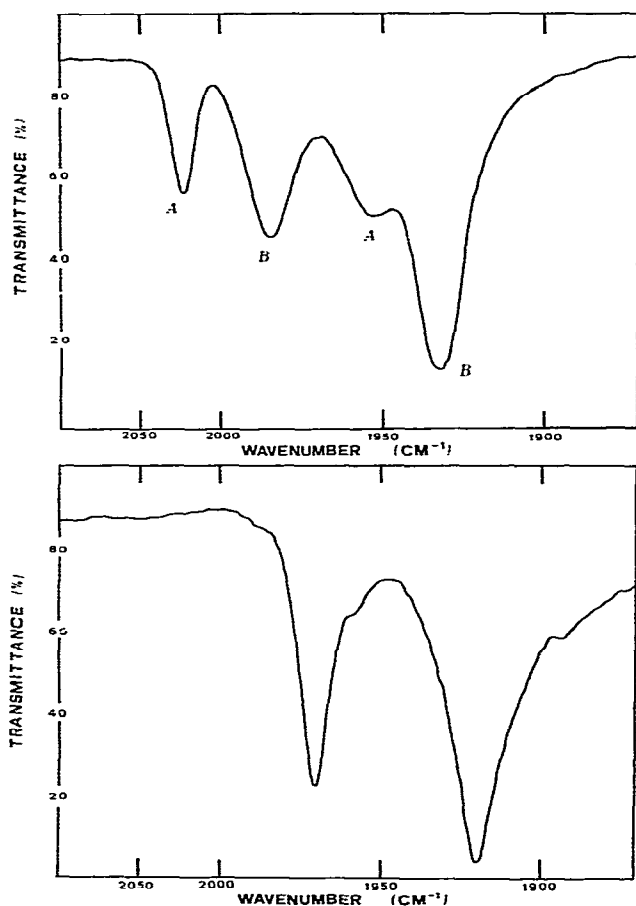
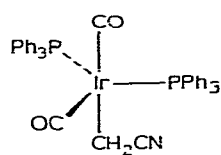
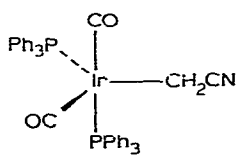


Fig. 2. IR spectrum of $\text{Ir}(\text{CH}_2\text{CN})(\text{CO})_2(\text{PPh}_3)_2$ in CH_2Cl_2 (upper) and in Nujol (lower).

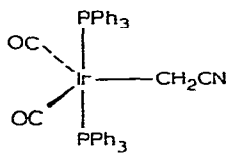
The possible solution structures are, thus, the configurations (1) and (2) for isomer A and (3) and (4) for isomer B, assuming only bipyramidal possibilities:



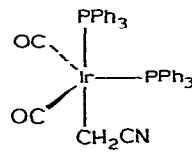
(1)



(2)



(3)



(4)

Attempts to discriminate between the possible molecular structures by ^1H NMR studies failed, since the resonance pattern of the methylene protons both in CD_2Cl_2 and deuteriotoluene at room temperature consists of a broad line which further broadens on cooling without approaching the slow limit even at -70°C . Studies at lower temperatures are precluded by crystallization. As a matter of fact, stereochemical non-rigidity is a common feature of five-coordinate chemistry.

Although the present data do not allow the unequivocal assignment of any individual configuration within the two pairs 1, 2 and 3, 4, the configurations 1 and 3 agree with the available evidence. Indeed, these structures represent a minimum modification of the parent structure, as the carbonyl and cyanomethyl groups in 1 as well as the two phosphine ligands in 3 retain their mutual *trans* position. They can thus best account for the very facile reversibility of the carbonylation reaction.

Finally, it has to be noted that the infrared spectrum of the solid (Fig. 2) closely resembles that of the solution isomer B; therefore the two forms are likely to possess the same ligand arrangement.

Reaction with oxygen

When solutions of complex I are left standing in the air, a dioxygen complex forms rapidly and irreversibly with a colour change from yellow to light-brown. The reaction also occurs in the solid phase, but some days are required for the oxygenation to proceed to an appreciable extent. We isolated the oxygen adduct, $\text{Ir}(\text{O}_2)(\text{CH}_2\text{CN})(\text{CO})(\text{PPh}_3)_2$ (III), in pure form from benzene as light-brown crystals in high yield. The formulation of III as an edge-on bonded O_2 complex is inferred from the infrared spectrum, which exhibits a strong absorption at 835 cm^{-1} . In addition, the carbonyl band, shifted by about 30 cm^{-1} above that of complex I, now lies in the frequency region observed for closely related dioxygen iridium complexes [12,20]. The ^1H NMR spectrum shows a methylene resonance split into a 1/2/1 triplet ($\tau = 8.12$; $J(\text{PH})$ 5 Hz). It is consistent with the presence of two equivalent phosphorus atoms but does not allow a decision on whether they are *cis* or *trans* to one another. However, since crystal structure determinations [21,22] have shown that the phosphine ligands adopt an axial position in the analogous adducts, $\text{Ir}(\text{O}_2)\text{X}(\text{CO})(\text{PPh}_3)_2$, complex III is very likely to possess the *trans* stereochemistry.

Reaction with perchloric and hexafluorophosphoric acids

Both of these concentrated acids react with complex I in acetonitrile to give the colourless hydrido cation, $[\text{IrH}(\text{CH}_2\text{CN})(\text{CH}_3\text{CN})(\text{CO})(\text{PPh}_3)_2]^+$ (IV), isolated as the white perchlorate (IVA) and hexafluorophosphate (IVB) salts. The reaction occurs almost immediately and can be easily reversed by strong bases such as tetraalkylammonium hydroxides. Conversely, the complex does not undergo reductive elimination of acetonitrile to give the stable $[\text{Ir}(\text{CH}_3\text{CN})(\text{CO})(\text{PPh}_3)_2]^+$ [23] except possibly under extreme conditions. The coexistence of Ir—H and Ir—C σ bonds in the same compound reflects the enhanced strength of the M—C bond in cyanoalkyl complexes with respect to those in analogous alkyl derivatives.

The ionic character of IVA and IVB has been confirmed by conductivity measurements in acetonitrile where they behave as 1/1 electrolytes.

The infrared spectra of the solids show, in addition to the bands of the uncomplexed anions, a strong carbonyl band and two medium intensity absorptions in the $2250\text{--}2210\text{ cm}^{-1}$ region assignable to $\nu(\text{C}\equiv\text{N})$ of the nitrile ligand and the cyanomethyl group. No band attributable to metal—hydrogen stretching is observed. $\nu(\text{Ir—H})$ is probably represented by one of the very weak bands in the $2300\text{--}2000\text{ cm}^{-1}$ region, but no unambiguous assignment can be made.

Evidence for the presence of a hydride ligand is provided, however, by the high field triplet observed in the ^1H NMR spectrum of IV ($\tau = 27.47$; $J(\text{PH})$ 12 Hz in CD_2Cl_2), the cyanomethyl protons appearing as a triplet ($\tau = 8.77$; $J(\text{PH})$ 9 Hz) and the methyl protons as a singlet ($\tau = 8.03$) in the appropriate integration ratio, and the mutual *trans* position of the phosphine ligands is also inferred. Again, the high value of the hydride chemical shift suggests that hydrogen is *trans* to a ligand of low *trans* influence [24] easily recognizable in the acetonitrile molecule; that the *trans* influence of the cyanomethanide ion is much higher than that of acetonitrile has been established for platinum(II) complexes [25]. Thus, the cation can be definitely assigned the configuration depicted in Fig. 1.

Acetonitrile is displaced from cation IV by triphenylphosphine to form $[\text{IrH}(\text{CH}_2\text{CN})(\text{CO})(\text{PPh}_3)_3]^+$ (V), isolated as the white hexafluorophosphate salt (VB). The reaction is reversible, but even in the presence of a large excess of the incoming ligand extended heating in dichloromethane under reflux is required to complete the substitution. Spectral evidence for the formation of V was also obtained from the reaction between complex I and $[\text{HPPH}_3]^+$ in CH_2Cl_2 .

Replacement of the CH_3CN by a PPh_3 ligand does not produce any substantial change in the infrared spectrum of the hydrido cation, with the obvious exception of the disappearance of the acetonitrile $\nu(\text{C}\equiv\text{N})$ band. In contrast, the ^1H NMR spectrum is greatly modified. The following main features are observed: (i) the hydride resonance, formerly a single triplet, appears markedly downfield as a widely separated pair of triplets at τ 21.44 ($J(\text{PH})$ *trans* 139 Hz; $J(\text{PH})$ *cis* 16 Hz); (ii) the triplet of the cyanomethyl protons is replaced by a

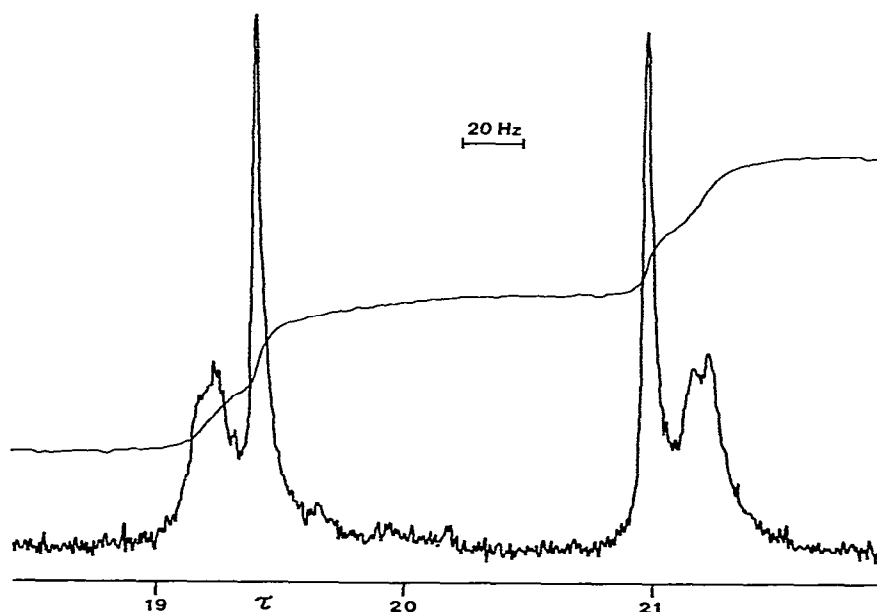


Fig. 3. High-field ^1H NMR pattern of $\text{IrH}_2(\text{CH}_2\text{CN})(\text{CO})(\text{PPh}_3)_2$. Isomer A.

near quartet at τ 8.40 ($J(\text{PH})$ *aver* ≈ 8 Hz) indicating coupling to three chemically similar phosphorus nuclei.

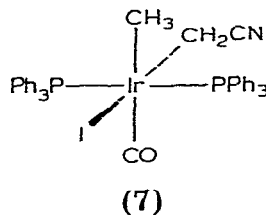
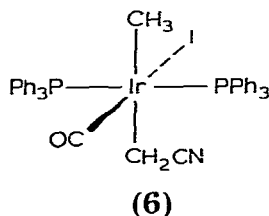
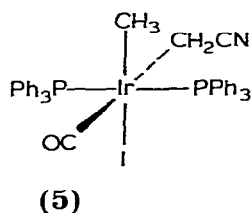
These results clearly indicate that the substitution involves retention of configuration.

Reaction with methyl iodide

Addition of a slight excess of methyl iodide to a solution of complex I in dichloromethane at room temperature discharges the yellow colour within a few minutes, and shifts the carbonyl band to higher frequencies ($\approx 50 \text{ cm}^{-1}$) as expected for the formation of an iridium(III) adduct. Air stable white crystals of a product are readily isolated from the solution in good yields and their elemental analysis, IR* and NMR data support the formulation $\text{IrI}(\text{CH}_2\text{CN})(\text{CH}_3)(\text{CO})\text{-(PPh}_3)_2$ (VI). It is noteworthy that VI provides an example of a stable iridium complex containing two metal-carbon σ bonds.

As far as the stereochemistry of the complex is concerned, the ^1H NMR spectrum shows two well resolved triplet resonances at τ 8.94 ($J(\text{PH})$ 8.5 Hz) and τ 9.68 ($J(\text{PH})$ 5 Hz) due to the methylene and methyl protons respectively, providing evidence for *trans* arrangement of the phosphine ligands.

Once the phosphines in the octahedral adduct are shown to be *trans*, three isomers are possible:



In order to elucidate the remaining stereochemistry we prepared the chloride complex analogous to VI by methathesis of the iodide derivative with lithium chloride in dichloromethane/methanol at room temperature. The far-infrared spectrum of this adduct (VII) reveals iridium-chlorine stretching absorption at 260 cm^{-1} corresponding, on the basis of Shaw's studies [26], to chlorine *trans* to methyl group. Since the iodide derivative VI can be recovered unchanged after heating under reflux for several hours in dichloromethane/methanol, while the halogen exchange is carried out at room temperature, isomerization processes are unlikely to be involved. Additional support for the improbability of isomerization is obtained by the ^1H NMR spectrum of VII, which shows the methyl resonance upfield from VI by an amount comparable with that found in analogous structurally well defined methyl halide iridium complexes [27].

Hence, the configuration of the adduct is established as depicted for 5.

Reaction with molecular hydrogen

The results so far described indicate that the complex *trans*- $\text{Ir}(\text{CH}_2\text{CN})(\text{CO})\text{-(PPh}_3)_2$

* The IR spectrum shows two CO stretching frequencies. This doublet is presumably due to solid-state splitting, since in CH_2Cl_2 there is only a single sharp peak.

$(\text{PPh}_3)_2$ is at least reactive towards adduct formation as Vaska's complex [6]. Hence, it was to be expected that complex I would react with molecular hydrogen or deuterium, and reaction does, indeed, occur readily at room temperature regardless of the solvent; the yellow colour of the complex lightens, and this is followed by separation of the white dihydride or dideuteride, $\text{IrH}_2(\text{or D}_2)(\text{CH}_2\text{CN})(\text{CO})(\text{PPh}_3)_2$ VIII or IX.

The infrared spectrum of both the hydride and deuteride shows a strong carbonyl band at 2004 cm^{-1} and a sharp absorption at 2205 cm^{-1} ascribable to $\text{C}\equiv\text{N}$ stretching of the cyanomethyl group. A medium intensity signal at 2102 cm^{-1} in VIII, shifted to 1505 cm^{-1} in IX, is assigned to $\text{Ir}-\text{H}$ stretching mode. Though a single hydrido band is observed, its high frequency value is indicative of *cis*-hydrides, the other expected band being likely far weaker and/or obscured [24]; it is relevant to note that oxidative addition of dihydrogen to metal complexes is acknowledged to occur, with a single and questionable exception [28], in a *cis* fashion. Each of these main vibrations, however, is occasionally coupled with a much weaker absorption at slightly lower frequencies, the relative intensity ratios varying from one preparation to another regardless of the solvent employed. A quite similar IR profile is shown in solution with the additional and significant feature of a slow but complete conversion of the higher frequency into the lower frequency set of bands. The white solid recovered from solutions allowed to stand long enough for completion of this conversion shows $\nu(\text{C}\equiv\text{N})$, $\nu(\text{Ir}-\text{H})$ and $\nu(\text{CO})$ at 2190 , 2090 and 1985 cm^{-1} , respectively. In the dideuteride the carbonyl stretching frequency has shifted to 2014 cm^{-1} suggesting that hydrogen is *trans* to CO. No deuterido band is observed, the $\text{Ir}-\text{D}$ frequency being obscured by the phosphine ligands.

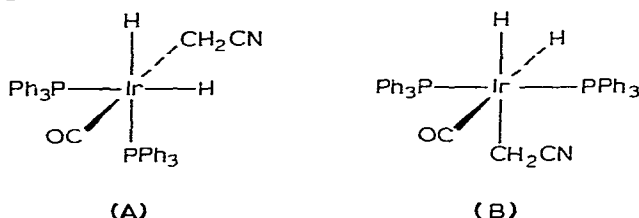
These observations infer the existence of two different isomeric adducts, A and B, of which species A is unstable in solution and slowly isomerizes to B*. Also, both isomers have the hydride ligands in mutually *cis* dispositions, a hydrogen being *trans* to carbonyl only in isomer B.

The complete structure assignments were based on ^1H NMR studies. The NMR spectrum run immediately after bubbling hydrogen for a few minutes through a solution of complex I in CD_2Cl_2 shows a centrosymmetrical high-field multiplet centered at τ 20.18 (Fig. 3). This resonance, characteristic of a system in which two hydrogens are mutually *cis* and are both *trans* to a phosphorus nucleus, is complex owing to the magnetic non equivalence of the two chemically equivalent protons [29]. A well resolved 1/2/1 triplet is observed at τ 9.53 ($J(\text{PH})$ 9 Hz) and assigned to the cyanomethyl protons. The absence of any other sizable hydrido resonance indicates that only isomer A is initially formed and, as a consequence, that the oxidative addition reaction of hydrogen to complex I is highly stereospecific. After the isomerization reaction is to complete, the NMR spectrum displays a pair of 1/2/1 triplets at τ 19.92 ($J(\text{PH})$ 18 Hz) and τ 22.34 ($J(\text{PH})$ 16 Hz) indicating that the phosphine ligands are mutually *trans*. The lower field triplet is due to the hydride *trans* to CO [24], the higher field one thus being attributable to the hydride *trans* to cyanomethyl

* The $\text{A} \rightarrow \text{B}$ isomerization in hydrogen-saturated dichloromethane was followed spectrophotometrically by monitoring the carbonyl band of both the appearing isomer B and the disappearing isomer A. The reaction was found to obey a first-order law with $t_{1/2} = 100\text{ min}$ at 25°C .

group. Indeed, evidence for the mutual *trans* position of CO and one H ligand had been previously provided by the D-labeling IR experiments (see above). The cyanomethyl protons still appear as a triplet resonance at τ 9.35 ($J(\text{PH})$ 5 Hz).

Hence, isomers A and B are unambiguously assigned the configurations depicted below:



The configuration of the thermodynamically favoured stereoisomer B appears once more to be that normally observed for *cis* additions to Vaska's complex and its analogues [6,30–33], the two bulky phosphine ligands maintaining the sterically more favourable mutual *trans* disposition. However, in spite of the thermodynamic stability of the isomer of configuration B, the hydrogen oxidative addition reaction follows a kinetic pathway greatly favouring the formation of the isomer of configuration A. Only a few examples of stereospecific oxidative additions to $\text{IrX}(\text{CO})\text{P}_2$ yielding products with *cis* phosphines have been so far reported, and the stereospecificity has been explained by a deformation of the square-planar complex on its approach to the transition state involving the migration of the phosphine ligands to positions *trans* to the incoming molecule and *cis* to each other, the X and CO ligands retaining, their colinear relationship to the metal [34–36]. Thus, the stereospecific course of the oxidative-addition of dihydrogen to *trans*- $\text{Ir}(\text{CH}_2\text{CN})(\text{CO})(\text{PPh}_3)_2$ could be due to the peculiarly favourable bonding situation in the $\text{OC}-\text{Ir}-\text{CH}_2\text{CN}$ skeleton, in which the high σ -donor capacity of the cyanomethanide ion is coupled with the high π -acceptor capability of the carbonyl ligand. It is noteworthy that addition of hydrogen to the complex *trans*- $\text{IrX}(\text{CO})(\text{PPh}_3)_2$, where X is a σ -bonded carborane, in solvents of moderate polarity similarly gives a primary product with stereochemistry analogous to A [13]. Steric crowding effects caused by the presence of the large carborane group would account for the non-stereospecificity of this reaction, in which a roughly equal amount of the isomer of configuration B is formed at the same time.

Finally, it is remarkable that, whereas the isomer of configuration A loses hydrogen simply on passing a stream of nitrogen through solutions at room temperature (50% conversion in about 30 min), the isomer of configuration B is quite stable under the same conditions. Indeed, prolonged bubbling of nitrogen in refluxing dichloroethane (several hours) is required for the reductive elimination reaction to occur to an appreciable extent.

Experimental

Chemicals and reagents

Commercial reagent grade chemicals were used without further purification.

The solvents were purified and dried by standard method and distilled under a current of nitrogen just before use.

trans-IrCl(CO)(PPh₃)₂ was prepared as previously reported [6].

Apparatus

The electrochemical apparatus and technique which were involved in the preparation of *trans*-Ir(CH₂CN)(CO)(PPh₃)₂ has been described previously [14]. Conductivities of 10⁻³ M solutions of complexes in acetonitrile at 25°C were measured with an LKB bridge. Infrared spectra were recorded on a Perkin—Elmer model 682 spectrometer; solution spectra were recorded with compensation in 0.5 or 1.0 mm CaF₂ liquid cells. Far-infrared spectra were taken on a Perkin—Elmer model 580B spectrometer. Electronic spectra were recorded on a Cary model 17D spectrometer. ¹H NMR spectra were recorded with a Varian FT-80A spectrometer.

Preparation of complexes

All preparations were carried out under nitrogen unless the use of hydrogen or carbon monoxide was required.

Chloroiodo(cyanomethyl)carbonylbis(triphenylphosphine)iridium(III) — IrClI(CH₂CN)(CO)(PPh₃)₂

Iodomethylcyanide (1.0 ml, 13.8 mmol) was added to a suspension of chloro-carbonylbis(triphenylphosphine)iridium(I) (1.22 g, 1.56 mmol) in dichloromethane (40 ml) and the mixture was stirred until complete dissolution (10–15 min). Upon the addition of diethyl ether, the product separated as very pale yellow powder, which was washed with diethyl ether and dried under vacuum (1.2 g, 80%). Anal. Found: C, 49.1; H, 3.45; N, 1.45. C₃₉H₃₂ClINOP₂Ir calcd.: C, 49.45; H, 3.40; N, 1.48%. Infrared absorption (nujol) occurred at 2216 (CN) and 2052 (CO) cm⁻¹.

(Cyanomethyl)carbonylbis(triphenylphosphine)iridium(I) — Ir(CH₂CN)(CO)-(PPh₃)₂ (I)

A suspension of IrClI(CH₂CN)(CO)(PPh₃)₂ (1.3 g, 1.37 mmol) in 20 ml of acetonitrile containing 0.1 M Et₄NClO₄ was electrolyzed under carefully deoxygenated argon at -2.0 V vs. Ag/0.1 M Ag⁺ acetonitrile electrode in a two-compartment cell on a mercury pool electrode. After completion of the electrolysis (two electrons/molecule of starting complex) the yellow crystalline precipitate was separated, washed with small amounts of cooled acetonitrile and dried under vacuum. The yield of isolated product was 80% (current yield 100%), but the remaining portion could be recovered from the spent catholyte by evaporation of the solvent under reduced pressure and subsequent extraction with benzene followed by addition of light petroleum.

(Cyanomethyl)dicarbonylbis(triphenylphosphine)iridium(I) — Ir(CH₂CN)(CO)₂(PPh₃)₂ (II)

A solution of Ir(CH₂CN)(CO)(PPh₃)₂ (0.2 g, 0.25 mmol) in dichloromethane (10 ml) was flushed with carbon monoxide at room temperature and atmospheric pressure until nearly colourless (1–2 min). A large volume of carbon

monoxide-saturated diethyl ether was added to precipitate the product, which was filtered off and dried under a stream of carbon monoxide (0.14 g, 70%).

Dioxygen(cyanomethyl)carbonylbis(triphenylphosphine)iridium(III) — Ir(O₂)(CH₂CN)(CO)(PPh₃)₂ (III)

A solution of Ir(CH₂CN)(CO)(PPh₃)₂ (0.2 g, 0.25 mmol) in benzene (10 ml) was stirred under dioxygen (1 atm) for 10 min. The colour changed from lemon-yellow to light-brown. Hexane was then added and the precipitate recrystallized from benzene/diethyl ether gave 0.17 g (80%) of light-brown crystals.

Hydrido(cyanomethyl)acetonitrilecarbonylbis(triphenylphosphine)iridium(III)-perchlorate and hexafluorophosphate — [IrH(CH₂CN)(CH₃CN)(CO)(PPh₃)₂]-ClO₄ (IVA) and [IrH(CH₂CN)(CH₃CN)(CO)(PPh₃)₂]PF₆ (IVB)

To the complex Ir(CH₂CN)(CO)(PPh₃)₂ (0.2 g, 0.25 mmol) in acetonitrile (5 ml) was added a few drops of concentrated perchloric acid. The solution immediately turned colourless. Upon the addition of diethyl ether, the product separated and was collected by filtration, washed with ether and air dried; Yield 0.19 g (85%).

The hexafluorophosphate salt was prepared similarly from HPF₆.

Hydrido(cyanomethyl)carbonyltris(triphenylphosphine)iridium(III)hexafluorophosphate — [IrH(CH₂CN)(CO)(PPh₃)₃]PF₆ (VB)

A mixture of 0.15 g (0.15 mmol) of [IrH(CH₂CN)(CH₃CN)(CO)(PPh₃)₂]PF₆ and 1.0 g (3.8 mmol) of triphenylphosphine in 20 ml of dichloromethane was heated at reflux for 5 h. The solution was allowed to cool at room temperature and the solvent stripped to a small volume at reduced pressure. Upon the addition of cyclohexane the crude product separated. Recrystallization from dichloromethane/pentane afforded 0.15 g (80%) of the white product.

Iodo(cyanomethyl)methylcarbonylbis(triphenylphosphine)iridium(III) — IrI(CH₂CN)(CH₃)(CO)(PPh₃)₂ (VI)

To 0.2 g (0.25 mmol) of Ir(CH₂CN)(CO)(PPh₃)₂ in dichloromethane (10 ml) was added an excess (0.2 ml, 3.2 mmol) of methyl iodide and the solution was stirred for 15 min. The solution was evaporated to dryness under reduced pressure. Recrystallization from dichloromethane/methanol afforded 0.15 g (70%) of white crystals.

Chloro(cyanomethyl)methylcarbonylbis(triphenylphosphine)iridium(III) — IrCl(CH₂CN)(CH₃)(CO)(PPh₃)₂ (VII)

Lithium chloride (2.0 g) was added to a solution of IrI(CH₂CN)(CH₃)(CO)(PPh₃)₂ (0.2 g, 0.22 mmol) in 50% v/v dichloromethane/methanol (40 ml) and the solution set aside for 2 days at room temperature. On cooling to -20°C the product separated as white prisms, which were washed with methanol and dried under vacuum (0.14 g, 77%).

Dihydrido(cyanomethyl)carbonylbis(triphenylphosphine)iridium(III) —
 $\text{IrH}_2(\text{CH}_2\text{CN})(\text{CO})(\text{PPh}_3)_2$ (VIII)

Isomer A

A stream of hydrogen was passed through a solution of $\text{Ir}(\text{CH}_2\text{CN})(\text{CO})(\text{PPh}_3)_2$ (0.2 g, 0.25 mmol) in dichloromethane (10 ml) at 0°C. The initially yellow colour lightened and in the course of 20 min a very pale yellow solution was obtained. Addition of cooled hexane precipitated a white solid, which was filtered off, washed with hydrogen-saturated hexane, and dried under a stream of hydrogen (0.16 g, 80%). According to spectroscopic data the product was the isomer of configuration A of such a purity that isomer B could not be detected.

The corresponding dideuteride IX was prepared similarly using deuterium.

Isomer B

A solution of 0.2 g (0.25 mmol) of $\text{Ir}(\text{CH}_2\text{CN})(\text{CO})(\text{PPh}_3)_2$ in 1,2-dichloroethane (10 ml) was heated at reflux for 1 h under a hydrogen atmosphere. The solution was allowed to cool at room temperature and the solvent stripped to a small volume in a stream of hydrogen. Careful addition of methanol induced crystallization. Upon standing overnight in the freezer, white crystals of the product were deposited (0.14 g, 70%).

Acknowledgement

We thank Mr. S. Sitran for technical assistance and Mr. F. Braga for running the NMR spectra.

References

- 1 G. Zotti, S. Zecchin and G. Pilloni, in preparation.
- 2 See for example: K. Suzuki, J. Ooyama and M. Sakurai, *Bull. Chem. Soc. Japan*, 49 (1976) 464; G. Oehme, K.C. Rober and H. Pracejus, *J. Organometal. Chem.*, 105 (1976) 127; R. Ros, R.A. Michelin, R. Bataillard and R. Roulet, *Ibid.*, 139 (1977) 355 and references quoted therein.
- 3 M. Lenarda and W.H. Baddley, *J. Organometal. Chem.*, 39 (1972) 217.
- 4 W.H. Baddley and P. Choudhury, *J. Organometal. Chem.*, 60 (1973) C74.
- 5 W. Beck, K. Schorpp, C. Oetker, R. Schlodder and H.S. Smedal, *Chem. Ber.*, 106 (1973) 2144.
- 6 L. Vaska and J.W. DiLuzio, *J. Amer. Chem. Soc.*, 83 (1961) 2784; L. Vaska, *Acc. Chem. Res.*, 1 (1968) 335.
- 7 F.D. Mango and I. Dvoretzky, *J. Amer. Chem. Soc.*, 88 (1966) 1654.
- 8 G. Yagupsky, C.K. Brown and G. Wilkinson, *J. Chem. Soc. A*, (1970) 1392.
- 9 R. Nast and L. Dahlenburg, *Chem. Ber.*, 105 (1972) 1436.
- 10 R.L. Bennett, M.I. Bruce and R.C.F. Gardner, *J. Chem. Soc. Dalton*, (1973) 2653.
- 11 M.D. Rausch and G.A. Moser, *Inorg. Chem.*, 13 (1974) 11.
- 12 L. Dahlenburg and R. Nast, *J. Organometal. Chem.*, 71 (1974) C49; *Ibid.*, 110 (1976) 395.
- 13 B. Longato, F. Morandini and S. Bresadola, *Inorg. Chem.*, 15 (1976) 650.
- 14 S. Zecchin, G. Schiavon, G. Pilloni and M. Martelli, *J. Organometal. Chem.*, 110 (1976) C45.
- 15 R. Brady, B.R. Flynn, G.L. Geoffroy, H.B. Gray, J. Peone and L. Vaska, *Inorg. Chem.*, 15 (1976) 1485.
- 16 R. Ros, J. Renaud and R. Roulet, *Helv. Chim. Acta*, 58 (1975) 133.
- 17 R. Ros, R.A. Michelin, G. Carturan and U. Belluco, *J. Organometal. Chem.*, 133 (1977) 213.
- 18 G. Yagupsky and G. Wilkinson, *J. Chem. Soc. A*, (1969) 725.
- 19 A. Reckziegel and M. Bigorgne, *J. Organometal. Chem.*, 3 (1965) 341.
- 20 C.A. Reed and W.R. Roper, *J. Chem. Soc. Dalton*, (1973) 1370.
- 21 S.J. LaPlaca and J.A. Ibers, *J. Amer. Chem. Soc.*, 87 (1965) 2581.
- 22 J.A. McGinnety, R.J. Doedens and J.A. Ibers, *Inorg. Chem.*, 6 (1967) 2243.
- 23 C.A. Reed and W.R. Roper, *J. Chem. Soc. Dalton*, (1973) 1365.
- 24 H.D. Kaesz and R.B. Saillant, *Chem. Rev.*, 72 (1972) 231 and references quoted therein.

- 25 R. Ros, J. Renaud and R. Roulet, *J. Organometal. Chem.*, 104 (1976) 393.
- 26 J.M. Jenkins and B.L. Shaw, *J. Chem. Soc.*, (1965) 6789.
- 27 A.J. Deeming and B.L. Shaw, *J. Chem. Soc. A*, (1969) 1128.
- 28 J.F. Harrod, G. Hamer and W. Yorke, *J. Amer. Chem. Soc.*, 101 (1979) 3987.
- 29 J.P. Jesson in E.L. Muetterties (Ed.), *Transition Metal Hydrides*, Marcel Dekker, New York, 1971 p. 75.
- 30 J.P. Collman, *Acc. Chem. Res.*, 1 (1968) 136.
- 31 J.P. Collman and W.R. Roper, *Adv. Organometal. Chem.*, 7 (1968) 53.
- 32 J. Halpern, *Acc. Chem. Res.*, 3 (1970) 386.
- 33 R. Ugo, A. Pasini, A. Fusi and S. Cenini, *J. Amer. Chem. Soc.*, 94 (1972) 7364.
- 34 J.F. Harrod and C.A. Smith, *J. Amer. Chem. Soc.*, 92 (1970) 2699.
- 35 J.F. Harrod, C.A. Smith and K.A. Than, *J. Amer. Chem. Soc.*, 94 (1972) 8321.
- 36 J.F. Harrod and W.J. Yorke, *Inorg. Chem.*, 20 (1981) 1156.