SYNTHESIS AND REACTIVITY OF SOME ISOCYANIDE COMPLEXES OF IRIDIUM(I)

KATSUHIKO KAWAKAMI, MASA-AKI HAGA and TOSHIO TANAKA

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-kami, Suita, Osaka (Japan)

SUMMARY

Several isocyanide complexes $[Ir(RNC)_4]X$ (I) ($R = p\text{-}CH_3C_6H_4$, $X = I$; $R = p\text{-}CH_3OC_6H_4$, $X = I$ and PF_6) and $[Ir(RNC)_2(PPh_3)_3]ClO_4$ (II) ($R = p\text{-}CH_3C_6H_4$ and $p\text{-}CH_3OC_6H_4$) have been prepared by the reactions of $[Ir(COD)Cl]_2$ and $[Ir(COD)(PPh_3)_2]ClO_4$ (COD = 1,5-cyclooctadiene) with arylisocyanides, respectively. Oxidative addition reactions of I and II with halogens, and II with π-acids such as tetracyanoethylene(TCNE), fumaronitrile, maleic anhydride, dimethyl fumarate, acrylonitrile, and dimethyl acetylenedicarboxylate are described. The structures of I, II and the π-acid addition products of II, $[Ir(p\text{-}CH_3C_6H_4NC)_2(PPh_3)_2(\pi\text{-acid})]ClO_4$ (IV) (π-acid = TCNE, fumaronitrile, maleic anhydride, and acetylene dicarboxylate), are discussed on the basis of their electronic, IR, and NMR spectra. Especially, I is suggested to have an unusual layer structure involving Ir to Ir interaction, the result of which is relatively low reactivity in oxidative addition reactions. Trigonal bipyramidal configurations are suggested for IV with the two isocyanides in the *trans* and *cis* positions for the olefin and acetylene adducts, respectively.

INTRODUCTION

A considerable amount of work has been carried out on the donor–acceptor interactions between basic transition metal complexes and various π-acids[1–4]. Very recently, renewed attention has been focused on synthesis, reactions, and structural chemistry of isocyanide complexes of rhodium(I)[5–13]. However, studies on isocyanide complexes of iridium(I) are relatively sparse[5,9,14].

We have recently reported that tetrakis(arylisocyanide)rhodium(I) perchlorates form adducts of square pyramidal configuration with TCNE, which is rotating freely in solution at room temperature[11]. In view of the fact that they are the first example of adducts of the kind formed between d^8 square-planar complexes and TCNE, it is of interest to extend the work to the analogous iridium(I) complexes. Here we report the novel synthesis and characterization of tetrakis(arylisocyanide)iridium(I) and bis-(arylisocyanide)tris(triphenylphosphine)iridium(I) complexes, and their adduct formation with halogens and various π-acids such as TCNE, fumaronitrile, maleic anhydride, dimethyl fumarate, acrylonitrile, and dimethyl acetylenedicarboxylate.

EXPERIMENTAL

Materials

Ammonium hexachloroiridate(IV), TCNE, and fumaronitrile were commercially available, and were used as supplied. Arylisocyanides[15] and μ-dichlorodi-π-1,5-cyclooctadienediiridium(I), [Ir(COD)Cl]$_2$[16] were prepared according to literature methods.

Preparation of complexes

π-*1,5-Cyclooctadienebis(triphenylphosphine)iridium(I) perchlorate*, [Ir(COD)-(PPh$_3$)$_2$]ClO$_4$

This compound was prepared in a manner similar to that described for [Rh(COD)(PPh$_3$)$_2$]ClO$_4$[17]. Sodium perchlorate monohydrate (2.95 g, 21 mmol) in H$_2$O (10 ml) was added to [Ir(COD)Cl]$_2$ (1.00 g, 1.5 mmol) in CH$_2$Cl$_2$ (10 ml) with vigorous stirring. Solid triphenylphosphine (2.90 g, 11.1 mmol) was added to the mixture, and the two-layer system was stirred vigorously for 15 min. The CH$_2$Cl$_2$ layer was separated and washed with two portions of H$_2$O (10 ml). The volume of the solution was reduced to about 5 ml under reduced pressure and to this was added ethanol (5 ml). Crystallization was effected by adding ether dropwise to yield red crystals of [Ir(COD)(PPh$_3$)$_2$]ClO$_4$ (2.65 g, 90%).

Tetrakis(arylisocyanide)iridium(I) iodide and hexafluorophosphate, [Ir(RNC)$_4$]X (I) (R = p-CH$_3$C$_6$H$_4$ and X = I (Ia); R = p-CH$_3$OC$_6$H$_4$ and X = I (Ib) and PF$_6$ (Ic))

p-Tolylisocyanide (0.39 g, 3.3 mmol) in CH$_2$Cl$_2$ (10 ml) was added slowly to [Ir(COD)Cl]$_2$ (0.30 g, 0.4 mmol) in CH$_2$Cl$_2$ (10 ml) and the mixture was stirred at room temperature for 1 h. The solvent was evaporated under reduced pressure and ethanol (10 ml) was added. Addition of NaI (0.24 g, 1.6 mmol) in ethanol (5 ml) to the solution yielded a dark green powder, which was reprecipitated from CH$_2$Cl$_2$ solution by the addition of petroleum ether to give Ia (0.25 g, 40%).

Ib (40%) and Ic (85%) were similarly obtained except that NH$_4$PF$_6$ in ethanol was used as the precipitating anion source in the case of Ic.

Bis(arylisocyanide)tris(triphenylphosphine)iridium(I) perchlorate, [Ir(RNC)$_2$-(PPh$_3$)$_3$]ClO$_4$ (II) (R = p-CH$_3$C$_6$H$_4$ (IIa) and p-CH$_3$OC$_6$H$_4$ (IIb))

p-Tolylisocyanide (0.37 g, 3.2 mmol) in acetone (10 ml) was added slowly to a mixture of [Ir(COD)(PPh$_3$)$_2$]ClO$_4$ (1.50 g, 1.6 mmol) and PPh$_3$ (0.41 g, 1.6 mmol) in acetone (10 ml). The solution was stirred for 1 h, during which time the color of the solution changed from red to orange. The solution was then concentrated under reduced pressure to 2 ml and to this was added ethanol (2 ml). Crystallization was effected by adding ether dropwise to yield yellow crystals of IIa, which were recrystallized from CH$_2$Cl$_2$–ether (75%). IIb(84%) was similarly obtained.

Oxidative addition reactions

Bis(p-tolylisocyanide)bis(triphenylphosphine)diiodoiridium(III)perchlorate, [Ir-(p-CH$_3$C$_6$H$_4$NC)$_2$(PPh$_3$)$_2$I$_2$] ClO$_4$ (III)

I$_2$(0.052 g, 0.2 mmol) in benzene was added to IIa (0.27 g, 0.2 mmol) in CH$_2$Cl$_2$

and the solution was stirred at ambient temperature for 15 min. The solution was concentrated under reduced pressure and crystallization was effected by adding petroleum ether. Recrystallization of the product from CH_2Cl_2–CH_3OH afforded orange yellow crystals of III.

Bis(p-tolylisocyanide)bis(triphenylphosphine)(π-acid)iridium(III)   perchlorate,   [Ir-(p-CH₃C₆H₄NC)₂(PPh₃)₂(π-acid)]ClO₄   (IV)   (π-acid = TCNE (IVa), fumaronitrile (IVb), maleic anhydride (IVc), dimethyl fumarate (IVd), acrylonitrile (IVe), and dimethyl acetylenedicarboxylate (IVf))

A small excess of solid TCNE (0.05 g, 0.4 mmol) was added to IIa (0.4 g, 0.3 mmol) in CH_2Cl_2 (10 ml) at room temperature. The solution was stirred for 15 min, during which time the yellow color faded. The solvent was evaporated under reduced pressure and the product was recrystallized from n-hexane–CH_2Cl_2 to yield white crystals of IVa (0.25 g, 70%). IVb (80%), IVc, and IVf (80%) were similarly obtained except that IVc was recrystallized from CH_2Cl_2–ether in the presence of maleic anhydride.

Although compounds IVd and IVe were not isolated and characterized, CH_2Cl_2 solutions of IIa containing excess dimethyl fumarate and acrylonitrile,

TABLE 1

COLOR AND ANALYTICAL DATA

Compound[a]	Color	Analysis: Found (Calcd.)(%)		
		C	H	N
Ia [IrL₄]I	Dark green	44.91	3.31	6.30
		(45.13)	(3.31)	(6.57)
Ib [IrL*₄]I·CH₂Cl₂[b]	Dark green	45.12	3.59	6.17
		(45.41)	(3.47)	(6.42)
Ic [IrL*₄]PF₆	Dark green	43.76	3.22	6.62
		(44.19)	(3.24)	(6.44)
IIa [IrL₂P₃]ClO₄	Yellow	63.31	4.83	2.23
		(64.04)	(4.53)	(2.13)
IIb [IrL*₂P₃]ClO₄·(CH₂Cl₂)₁/₂[b]	Yellow	61.46	4.46	2.10
		(61.04)	(4.36)	(2.02)
III [IrL₂P₂I₂]ClO₄	Orange yellow	48.01	3.42	2.36
		(47.88)	(3.40)	(2.15)
IVa [IrL₂P₂(TCNE)]ClO₄	White	58.56	3.42	2.36
		(59.11)	(3.76)	(2.13)
IVb [IrL₂P₂(FN)]ClO₄	White	59.36	4.26	4.96
		(59.60)	(4.11)	(4.96)
IVc [IrL₂P₂(MA)]ClO₄	White	58.05	4.05	2.41
		(58.56)	(4.04)	(2.44)
IVf [IrL₂P₂(DAD)]ClO₄	White	58.16	4.18	2.49
		(58.41)	(4.23)	(2.35)

[a] The abbreviations used are as follows: L = p-CH₃C₆H₄NC, L* = p-CH₃OC₆H₄NC, P = PPh₃, TCNE = tetracyanoethylene, FN = fumaronitrile, MA = maleic anhydride, and DAD = dimethyl acetylenedicarboxylate.

[b] Presence of CH_2Cl_2 was confirmed by ¹H NMR spectra.

TABLE 2

RELEVANT IR(cm⁻¹) AND ¹H NMR(ppm) DATA

Compound[a]	IR[b]		¹H NMR[c]		
	$\nu(N\equiv C)$	Others	τ(phenyl)	$\tau(CH_3$ or $CH_3O)$	Others
Ia [IrL₄]I	2145		(3.52(broad))	(6.28(broad))	
Ib [IrL*₄]I·CH₂Cl₂	2153		(3.52(broad))	(7.77(broad))	
IIa [IrL₂P₃]ClO₄	2119(2123)		(3.00 4.13(q))	(7.79)	
IIb [IrL*₂P₃]ClO₄·(CH₂Cl₂)₁/₂	2125(2126)		(3.26 4.04(q))	(6.28)	
IVa [IrL₂P₂(TCNE)]ClO₄	2196(2196)	$\nu(C\equiv N)$ (2226)	2.88 3.41 (q)	7.58	
IVb [IrL₂P₂(FN)]ClO₄	2174(2175)	$\nu(C\equiv N)$ (2216)	2.95 3.57(q)	7.60	τ(FN) 7.22
IVc [IrL₂P₂(MA)]ClO₄	2171(2172)		3.06 3.67(q)	7.66	τ(MA) 6.06
			2.96 3.60(q)	7.63	
IVf [IrL₂P₂(DAD)]ClO₄	2175(2173) 2140(2139)	$\nu(C\equiv C)$ (1772)	3.02 3.67(q)	7.68	τ(DAD) 6.58

[a] The abbreviations used are as follows: L = p-CH₃C₆H₄NC, L* = p-CH₃OC₆H₄NC, TCNE = tetracyanoethylene, FN = fumaronitrile, MA = maleic anhydride, and DAD = dimethyl acetylenedicarboxylate. [b] Measured in Nujol mulls (in CH₂Cl₂). [c] Measured in CDCl₃ (in DMSO-d_6). [d] The coupling constants of AB type quartets(q) for phenyl ring protons are all about 8 Hz.

respectively, were investigated by means of IR and ^{1}H NMR spectra in order to obtain information concerning their existence in solution.

Table 1 shows the colors and analytical data of the complexes prepared.

Instrumentation

Molecular weights were determined in CH_3CN at 37° by using a Mechrolab vapor pressure osmometer. The electric conductivity was measured in CH_3CN solutions by using a Yokogawa F-255A Universal Bridge and a cell with the cell constant of 0.322 cm^{-1}. CH_3CN was distilled over P_2O_5 several times. IR spectra were obtained as Nujol mulls and in $CDCl_3$ or CH_2Cl_2 solutions on a Hitachi–Perkin–Elmer 225 grating spectrophotometer. ^{1}H NMR spectra were recorded in 2.5 to 5.0 wt % $CDCl_3$, CH_2Cl_2, or dimethyl sulphoxide-d_6 (DMSO-d_6) solutions on a JNM-PS-100 Spectrometer operating at 100 MHz. ^{31}P NMR spectra were recorded in 22 wt % solutions at 40 MHz on the same spectrometer. Internal tetramethylsilane and external 85 % H_3PO_4 were used as reference compounds.

IR and ^{1}H NMR spectral data are given in Table 2.

RESULTS AND DISCUSSION

Preparation of arylisocyanide complexes of iridium(I)

Although a few tetrakis(*p*-tolylisocyanide)iridium(I) complexes [Ir(*p*-CH$_3$-C$_6$H$_4$NC)$_4$]X (X = Br, I, and ClO$_4$) have been known for some time[5], their syntheses are not necessarily simple and convenient. We have now found that reactions of a stoichiometric amount of arylisocyanides with [Ir(COD)Cl]$_2$[16], followed by the addition of appropriate anions, easily give the desired product [Ir(RNC)$_4$]X (I) (R = *p*-CH$_3$C$_6$H$_4$ and X = I (Ia); R = *p*-CH$_3$OC$_6$H$_4$ and X = I (Ib) and PF$_6$ (Ic)). During the course of our investigation, a communication by McCleverty *et al.*[9] appeared, which gave a brief account of the preparation of cationic isocyanide complexes of Ir^I starting from dicyclooctenechlorocarbonyliridium(I). Another communication by Bedford and Rouschias[14] reported the preparation of [Ir-(CH$_3$NC)$_4$]$^+$ salts starting from Ir(PPh$_3$)$_2$(CO)Cl and CH$_3$NC and their photochemical reactions, which will be referred to later.

Several attempts were made to prepare four-coordinate [Ir(RNC)$_2$(PPh$_3$)$_2$]-ClO$_4$ by the reaction between [Ir(COD)(PPh$_3$)$_2$]ClO$_4$ and two equivalents of RNC. Only low yields of impure complexes were obtained, with red material remaining. However, five-coordinate [Ir(RNC)$_2$(PPh$_3$)$_3$]ClO$_4$ (II) was obtained pure in almost quantitative yield, when the reaction was carried out in the presence of one equivalent of PPh$_3$. In contrast, McCleverty *et al.*[9] reported, without experimental details, the isolation of either [Ir(RNC)$_2$(PPh$_3$)$_2$]Cl (R = i-Pr or *p*-ClC$_6$H$_4$) or [Ir(RNC)$_3$-of PPh$_3$. In contrast, McCleverty *et al.*[9] reported, without experimental details, the Ir(PPh$_3$)$_2$(CO)Cl,

Reactivity and structure of [Ir(RNC)$_4$]X (I)

Solid samples of I are very stable to air and well characterized by the elemental analysis. I in solution does undergo photochemical reactions when irradiated with visible light, to show a color change from dark green to orange. However, the reaction rate is drastically lower than that of the methyl isocyanide analogue[14], whose solutions

are reported to turn red or orange in light within minutes. No information suggesting the presence of the solvated complex $[Ir(p\text{-}CH_3OC_6H_4NC)_4(CH_3CN)]I$ is obtained by ^1H NMR spectra of an orange sample, which is produced by irradiating Ib in CH_3CN. These features of I are in a sharp contrast to those of the methyl isocyanide analogues reported to be oxidized instantaneously by air, even as solids. They are also reported to undergo photoassociation reactions to give $[Ir(CH_3NC)_4(solvent)]X$ compounds easily, when irradiated with visible light. In the absence of oxygen, they give intense blue solutions in various solvents (λ_{max} 610±20; ε 22000). The origin of these bands is implicitly suggested to be essentially the metal to ligand charge transfer. However, the bands are also possibly due to the Ir to Ir interaction.

Ia reacts with Cl_2 and Br_2 to give oxidative addition products. However, I does not react with TCNE, which is known to form adducts with tetrakis(arylisocyanide)rhodium(I) perchlorates[11]. This fact is surprising in view of the strong tendency of low-valent transition metal complexes to undergo oxidative addition reactions[2]. The limited reactivity of I toward TCNE, however, is consistent with an assumption that I has Ir to Ir interaction, even in solution, as is illustrated in the following discussions.

I is remarkably deep in color and is sparingly soluble in non-polar solvents. Molecular weights of Ia, Ib, and Ic in 1.9, 3.0, and 2.0 wt% CH_3CN solutions are 1583, 3115, and 3368, respectively. These data suggest that the complex salts I exist as oligomers, even in solution.

Conductivity of I shows some concentration and time dependence. Thus, conductivity of Ib in 10^{-3} and 10^{-4} M CH_3CN solutions, when protected from light and measured immediately after the preparation of the solution, is 67 and 97 $ohm^{-1} \cdot mol^{-1} \cdot cm^2$, respectively. Conductivity of the 10^{-4} M solution increases to be 99 and 106 $ohm^{-1} \cdot mol^{-1} \cdot cm^2$, after 2 and 24 hours, respectively. The change in conductivity is not much, even when measurements are carried out on samples exposed to light. Conductivity is tentatively calculated in the unit of $ohm^{-1} \cdot mol^{-1} \cdot cm^2$, assuming that I exists as the monomer $[Ir(RNC)_4]X$. Molecular weight determinations at concentrations parallel to those for conductivity measurements are unreliable because of too low concentration, which makes it impossible to know the degree of association of I in solution, e.g., whether I exists as either $[Ir(RNC)_4]X$, $[Ir_2(RNC)_8]X_2$, or $[Ir_3(RNC)_{12}]X_3$ etc. Therefore, although some change in conductivity is observed for I, these data do not offer much information on the nature of I in solution, except showing that I is ionic as formulated.

In the ^1H NMR spectra of Ib and Ic in DMSO-d_6, both the phenyl ring and methoxy protons appear as broad singlets in spite of a sharp signal for tetramethylsilane. The broad appearance of these signals is neither altered at temperatures to 100° nor changed by the addition of the appropriate free isocyanide, which precludes the possibility of ligand exchange in solution. Broad signals are still observable with an orange sample, which is obtained by irradiating Ib with visible light in CH_3CN. The reason for this is not clear.

On the other hand, the electronic spectra of Ib in 10^{-3} and 10^{-4} M CH_3CN solutions show remarkable light, concentration, and time dependence. Thus, the spectrum of Ib in 10^{-3} M solution, when prepared in the dark and measured immediately after the preparation of the solution, shows a distinct absorption maximum at 712 nm (ε 1.2 × 10^4), which does not change much in the dark. This band, in light,

gradually decreases in intensity and is finally replaced, after 15 h, by new shoulders around 580 nm ($\varepsilon 1 \times 10^3$) and 440 nm ($\varepsilon 2 \times 10^3$). The band at 712 nm disappears more quickly with lower concentrations. Similar behaviors are observed with Ia and Ic, which also have maxima at 720 nm ($\varepsilon 1.1 \times 10^4$) and 715 nm ($\varepsilon 1.3 \times 10^4$), respectively. Moreover, an absorption maximum is observed at 715 nm for Ic in the solid state. Appearance of these bands with large ε values in the long wavelength region is strongly indicative of the presence of Ir to Ir interaction in $[Ir(RNC)_4]^+$ cations. Metal to metal interaction is well characterized in some square-planar platinum metal complexes, which are significantly deep colored, on the basis of X-ray crystallographic analysis and comparison of the solid and solution electronic spectra[18]. One of the typical examples is the various salts of tetracyanoplatinum(II) complex anion $[Pt(CN)_4]^{2-}$, which show a characteristic absorption band beyond 500 nm in their polarized spectra parallel to the crystal axes. The band is known to shift to the longer wavelength, the shorter the Pt–Pt distance is. Although most of these salts do not show any absorption indicative of metal to metal interaction in solution, $Be[Pt(CN)_4]\cdot 4H_2O$ dissolves in CH_3OH to show color changes from colorless to yellow and finally to orange yellow with increasing concentrations[18b]. Comparison of the electronic spectral change and the color change with concentration of $[Pt(CN)_4]^{2-}$ with those of I seems to indicate that I retains the metal to metal interaction for longer time in solution. The disappearance of the absorption maximum of I around 720 nm may be explained in terms of the Ir to Ir chain breaking induced by light.

Based on the results described above, we suggest that $[Ir(RNC)_4]^+$ cations may exist as oligomers with Ir to Ir interaction not only in the solid state but also in solution for some time. However, the Ir to Ir chain may be slowly broken by photochemical reactions, which are shown to occur in $[Ir(CH_3NC)_4]X$ remarkably rapidly[14]. This may be the first example of metal to metal interaction occurring between cations. Recently Ir to Ir interaction between neutral complexes has been suggested for acetylacetonatodicarbonyliridium(I)[19]. Interactions between anions and cations, and between anions are well known for some square-planar complexes[18].

Reactivity of $[Ir(p\text{-}CH_3C_6H_4NC)_2(PPh_3)_3]ClO_4(IIa)$ with various π-acids

Only one strong and broad $N\equiv C$ stretching band is observed for $[Ir(RNC)_2$-$(PPh_3)_3]ClO_4$ (II) ($R = p\text{-}CH_3C_6H_4$ (IIa) and $p\text{-}CH_3OC_6H_4$ (IIb)) in CH_2Cl_2 solution. Their ^1H NMR spectra in DMSO-d_6 show one sharp singlet for the methyl and methoxy protons and only one set of AB type quartet for the isocyanide ring protons for IIa and IIb, respectively. The ^{31}P NMR spectrum of IIa in CH_2Cl_2 shows only one signal at 0.0 ppm from the external H_3PO_4. Addition of one equivalent of free phosphine to the solution slightly shifts the signal to the lower field (-0.9 ppm) with a distinct signal still observable for the free phosphine (5.3 ppm). In view of these results, the cationic part of IIa undergoes phosphine exchange to make the three phosphines magnetically equivalent on the NMR time scale. Therefore, the configuration of II may be either a trigonal bipyramid or a tetragonal pyramid, both with the two isocyanides in the *trans* position, in which the three phosphines are exchanging with one another to some extent. Rearrangement between two configurations is also possible. In $CDCl_3$, however, II shows other sets of weak ^1H NMR signals for the isocyanides (not due to the free ligand), which might be due to some oxidative addition

products of II with the solvent molecules.

IIa reacts with I_2 to give $[Ir(p-CH_3C_6H_4NC)_2(PPh_3)_2I_2]ClO_4$ (III) with dissociation of one molecule of PPh_3. IIa also reacts with four π-acids in CH_2Cl_2 to yield stable adducts $[Ir(p-CH_3C_6H_4NC)_2(PPh_3)_2(\pi\text{-acid})]ClO_4$ (IV) (π-acid = TCNE (IVa), fumaronitrile (IVb), maleic anhydride (IVc), and dimethyl acetylene-dicarboxylate (IVf)), with dissociation of one molecule of PPh_3, whose configurations will be discussed later. On the other hand, reactions of IIa with dimethyl fumarate and acrylonitrile lead only to recovery of the starting materials. In the latter two cases, however, formation of adducts in solution is shown by their IR and ^1H NMR spectra.

For IVa and IVb, observation of only one $N\equiv C$ stretching vibration and magnetic equivalence of two sets of phenyl ring protons for the isocyanide ligands (Table 2) favor the configuration A and B in Fig. 1. The square pyramidal configuration B with the cyanoolefins in the apical site, which is analogous to that reported by us recently for $[Rh(RNC)_4(TCNE)]ClO_4$ ($R = p\text{-}CH_3C_6H_4$, $p\text{-}CH_3OC_6H_4$, $p\text{-}ClC_6H_4$, and $o\text{-}CH_3C_6H_4$)[11], is not likely here, because IVa and IVb show little change in their ^1H NMR spectra in $CDCl_3$ in the temperature range between $-30°$ and $+55°C$. If they took the configuration B, it would be possible that the cyanoolefins might be rotating freely to give some temperature-dependent ^1H NMR spectra. Moreover, the fact that IIa reacts even with dimethyl fumarate and acrylonitrile to some extent in solution suggests that the basicity of the reactive species of IIa may be comparable with that of Vaska's complex, of which the TCNE and fumaronitrile adducts are known to have the cyanoolefins coordinated rigidly[20,21]. Thus, the cyanoolefin adducts of IIa may be concluded to have the configuration A.
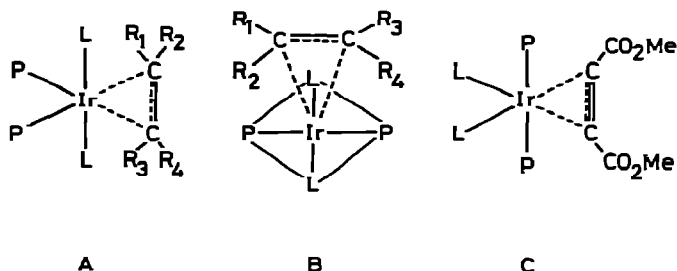

Fig. 1. Configurations of complexes. A, B, and C: $L = p\text{-}CH_3C_6H_4NC$ and $P = PPh_3$. A-1: $R_1 = R_2 = R_3 = R_4 = CN$ (IVa); A-2: $R_1 = R_4 = H$, $R_2 = R_3 = CN$ (IVb); A-3: $R_1 = R_3 = CO_2CO$, $R_2 = R_4 = H$ (IVc).

The fumaronitrile adduct IVb exhibits a novel olefinic proton resonance pattern, as is shown in Fig. 2. This resonance pattern can be interpreted as the AA'XX' system, which is due to the spin–spin coupling between the olefinic protons and two phosphorus nuclei[22]. On the basis of a simple calculation assuming the configuration A in Fig. 1, the coupling constants of the olefinic protons with trans- and cis-phosphorus are about 3 and 1 Hz, respectively. This result indicates that the iridium–fumaronitrile bonding in IVb contains significant σ-character.

The IR spectrum of IVc in CH_2Cl_2 shows only one $N\equiv C$ stretching band (Table 2), suggesting that the configuration of IVc may be also A similar to those of IVa and IVb. Another proof for the configuration comes from the fact that the ^1H
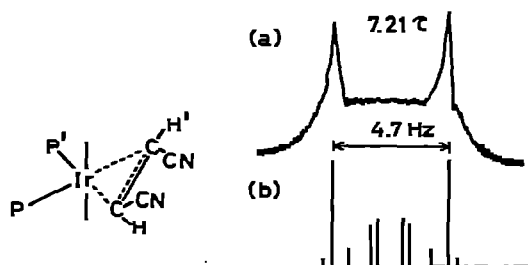
Fig. 2 The ^{1}H NMR Spectrum for the olefinic protons of $[Ir(p\text{-}CH_3C_6H_4NC)_2(PPh_3)_2(\text{fumaronitrile})]ClO_4$. (a) The observed spectrum; (b) The calculated spectrum as an AA'XX' system assuming $^1J(P\text{-}P)$ 1.5, $^3J(H\text{-}H')$ 0.5, $^3J(P\text{-}H)$ 1.3, and $^3J(P\text{-}H')$ 3.4 Hz.

NMR spectrum shows the existence of two kinds of isocyanide ligands, which are possibly due to the diamagnetic anisotropy of the carbonyl groups of the maleic anhydride. Thus, six distinct signals are observed for the phenyl ring protons of the isocyanides in the region between τ3 and 4 ppm (Table 2). These six signals can be explained to be due to the overlap of two sets of approximate AB type quartets. In accordance with this, the methyl protons are also split and the signal for the coordinated maleic anhydride appears at τ6.06 ppm ($|J|$ 3.5 Hz). Integration of the isocyanide protons and those of the coordinated maleic anhydride confirms the 1 to 1 adduct formation. The coordinated maleic anhydride protons of IVc show an essentially similar resonance pattern as that of the fumaronitrile adducts IVb depicted in Fig. 2. However, in this case, the splitting is not large enough to allow the calculation of the coupling constants.

Figure 3 shows the IR spectra of IIa in the presence of an excess of dimethyl fumarate in the $\nu(N\equiv C)$ region. The new band at 2173 cm^{-1}, which is 50 cm^{-1} higher than that of the free IIa, can be attributed to adduct formation, possibly with dis-
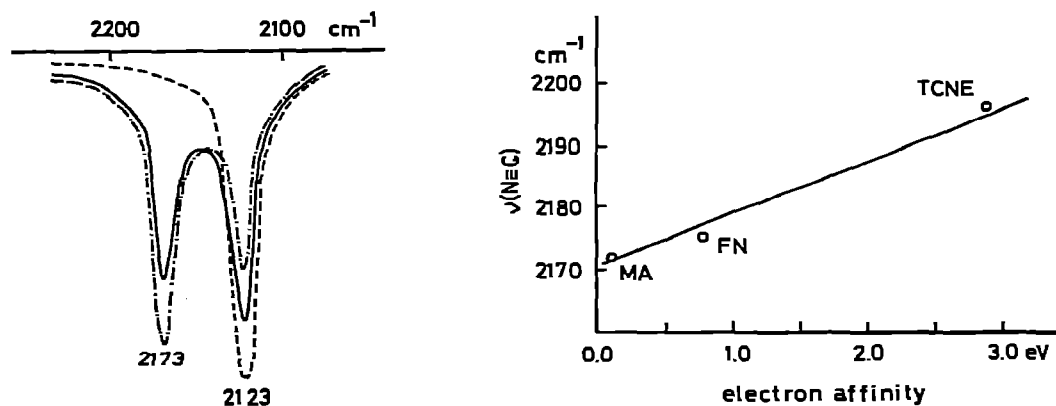

Fig. 3. The IR spectra of $[Ir(p\text{-}CH_3C_6H_4NC)_2 (PPh_3)_3]ClO_4$ (IIa) with and without dimethyl fumarate (DF) in CH_2Cl_2. Molar ratio DF/IIa: 0------; 1————; 5—·—·—·—

Fig. 4. A relationship between the $\nu(N\equiv C)$ of the olefin adducts $[Ir(p\text{-}CH_3C_6H_4NC)_2 (PPh_3)_2 (\text{olefin})]ClO_4$ and the electron affinity of the olefins (TCNE = tetracyanoethylene, FN = fumaronitrile, and MA = maleic anhydride).

sociation of one molecule of PPh₃. A similar new band is observed at 2157 cm⁻¹ in the case of acrylonitrile. Thus, IIa is shown to form adducts to some extent, even with dimethyl fumarate and acrylonitrile in solution.

A crude linear relationship is obtained between the $\nu(N\equiv C)$ of the olefin adducts of IIa in CH_2Cl_2 (olefin = TCNE, fumaronitrile, and maleic anhydride) and the electron affinity of the olefins[23], and this is shown in Fig. 4. The relationship shows that back donation from the iridium atom to the isocyanides decreases as the electron affinity of the olefin increases. Similar results have been found for the $\nu(CO)^{1-3}$ of some adducts with Vaska's complex and for the $\nu(N\equiv C)^{24}$ of some nickel and palladium isocyanide complexes.

IIa reacts with dimethyl acetylenedicarboxylate to give the white complex IVf, whose IR spectrum in CH_2Cl_2 solution shows, in a sharp contrast to those of the olefin adducts two strong $\nu(N\equiv C)$ bands (Table 2). This is due to the two isocyanides located in the *cis*-position with each other. The ¹H NMR spectrum shows only one set of *AB* type quartet for the isocyanides and a sharp singlet for the carbomethoxy protons of the acetylene; this is consistent with configuration C (Fig. 1). Two further bands are observed at 1772 and 1692 cm⁻¹, which are assigned to $\nu(C\equiv C)$ and the ester $\nu(C=O)$ bands, respectively. The $\nu(C\equiv C)$ is lower by about 400 cm⁻¹ than that of the free acetylene. Thus, the IR–acetylene bond in IVf is assumed to contain significant σ-character (Fig. 1c). May *et al.*[25] reported $\nu(C\equiv C)$ at 1814 cm⁻¹ for an isostructural CO complex, $[Ir(CO)_2(PPh_3)_2[C_2(CO_2CH_3)_2]]BPh_4$. The larger decrease in $\nu(C\equiv C)$ frequency of the isocyanide complex compared with that of the corresponding CO complex may be interpreted in terms of the strong σ-donating and less π back-bonding capacity of the isocyanide ligand. It is also noteworthy that, with IIa, the olefins such as TCNE, fumaronitrile, and maleic anhydride, and dimethyl acetylenedicarboxylate selectively form adducts of different configurations A and C in Fig. 1, respectively.

REFERENCES

1 D. F. Shriver, *Accounts Chem. Res.*, 3 (1970) 231.
2 J. P. Collman, *Accounts Chem. Res.*, 1 (1968) 136.
3 L. Vaska, *Accounts Chem. Res.*, 1 (1968) 335.
4 W. H. Baddley, *Inorg. Chim. Acta Rev.*, 2 (1968) 7.
5 L. Malatesta and F. Bonati, *Isocyanide Complexes of Metals*, Wiley, New York, 1969.
6 T. Boshi, P. Uguagliati, and B. Crociani, *J. Organometal. Chem.*, 30 (1970) 283.
7 A. Nakamura, Y. Tatsuno, Y. Yamamoto, and S. Otsuka, *J. Amer. Chem. Soc.*, 93 (1971) 6052.
8 A. L. Balch and J. Miller, *J. Organometal. Chem.*, 32 (1971) 263.
9 J. W. Dart, M. K. Lyoyd, J. A. McCleverty and R. Mason, *Chem. Commun.*, (1971) 1197.
10 R. V. Parish and P. G. Simms, *J. Chem. Soc., Dalton*, (1972) 809.
11 K. Kawakami, T. Kaneshima and T. Tanaka, *J. Organometal. Chem.*, 34 (1972) C21.
12 P. R. Brason and M. Green, *J. Chem. Soc., Dalton*, (1972) 1303.
13 A. Nakamura, Y. Tatsuno and S. Otsuka, *Inorg. Chem.*, 11 (1972) 2058.
14 W. M. Bedford and G. Rouschias, *Chem. Commun.*, (1972) 1224.
15 T. Shingaki and M. Takebayashi, *Bull. Chem. Soc. Japan*, 36 (1963) 617.
16 G. Winkhaus and H. Singer, *Chem. Ber.*, 99 (1966) 3610.
17 R. R. Shrock and J. A. Osborn, *J. Amer. Chem. Soc.*, 93 (1971) 2397.
18 (a) K. K. Krogmann, *Angew. Chem. Intern. Edit.*, 8 (1969) 35; (b) S. Yamada, *Kagaku (Iwanami)*, 41 (1971) 651; (c) T. W. Thomas and A. E. Underhill, *Chem. Soc. Rev.*, 1 (1972) 99.

19 (a) L. K. Monteith, L. F. Ballard, C. G. Pitt, *Solid State Commun.*, 6 (1968) 301; (b) C. G. Pitt, L. K. Monteith, L. F. Ballard, J. P. Collman, J. C. Morrow, W. R. Roper and D. Ulku, *J. Amer. Chem. Soc.*, 88 (1966) 4286.
20 W. H. Baddley, *J. Amer. Chem. Soc.*, 90 (1968) 3705.
21 (a) J. A. McGinnety and J. A. Ibers, *Chem. Commun.*, (1968) 235; (b) L. M. Muir, K. W. Muir and J. A. Ibers, *Disc. Faraday Soc.*, 47 (1969) 84.
22 J. W. Emsley, J. Feeney and L. H. Sutcliffe, *High Resolution Nuclear Magnetic Resonance Spectroscopy*, Pergamon Press, New York, 1965, p. 392.
23 (a) A. C. Farragher and A. M. Page, *Trans. Faraday Soc.*, 63 (1967) 2369; (b) C. H. Wells, *Tetrahedron*, 22 (1966) 1985.
24 S. Otsuka, T. Yoshida and Y. Tatsuno, *J. Amer. Chem. Soc.*, 93 (1971) 6462.
25 M. J. Church, M. J. Mays, R. N. F. Simpson and F. P. Stefanini, *J. Chem. Soc. (A)*, (1970) 2909.