Title	STUDIES ON THE ACTIVATION OF OLEFINS AND ACETYLENES BY RHODIUM(Ⅰ) AND IRIDIUM(Ⅰ) COMPLEXES
Author(s)	芳賀, 正明
Citation	大阪大学, 1977, 博士論文
Version Type	VoR
URL	https://hdl.handle.net/11094/2765
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STUDIES ON THE ACTIVATION OF OLEFINS AND ACETYLENES BY RHODIUM(I) AND IRIDIUM(I) COMPLEXES

1976

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PREFACE

This thesis was performed under the guidance by Professor Toshio Tanaka at the Department of Applied Chemistry, Faculty of Engineering, Osaka University.

I would like to express my sincere thanks to Professor Toshio Tanaka for his invaluable guidance and constant encouragement throughout this work.

I am also very grateful to Dr. Katsuhiko Kawakami for his valuable guidance and encouragement from the beginning of the work. I equally make grateful acknowledgements to Dr. Gen-etsu Matsubayashi, Dr. Koji Tanaka, and Dr. Tokitaka Kaneshima for their helpful suggestions and discussions.

It is a real pleasure to express my gratitude to Mr. Hiroshi Yukawa for his collaboration in a part of the present study. I wish to thank all the members of Tanaka laboratory for their friendship.

I am indebted to Professor Yoshiharu Izumi, at the Institute for Protein Research, Osaka University for his helpful guidance and letting me use the polarimeter.

Finally the heartful thanks and appreciation are also extended to my parents for their understanding and constant encouragement.

Masaaki Haga

Masa-aki Haga

Suita, Osaka

December, 1976

LIST OF PAPERS

The contents of this thesis are composed of the following papers.

(1) Synthesis and Reactivity of Some Isocyanide Complexes of Iridium(I).
Katsuhiko Kawakami, Masa-aki Haga, and Toshio Tanaka,
J. Organometal. Chem., 60, 363 (1973).

(2) Kinetics of the Addition Reactions of Tetracyanoethylene towards Rhodium(I) Cationic Isocyanide Complexes.
Masa-aki Haga, Katsuhiko Kawakami, and Toshio Tanaka,
Inorg. Chim. Acta, 12, 93 (1975).

(3) Kinetics of the Addition of Tetracyanoethylene to Bis(tertiary phosphine)bis(isocyanide) Rhodium(I) Perchlorates.
Toshio Tanaka, Masa-aki Haga, and Katsuhiko Kawakami,
Organotransition-Metal Chemistry, edited by Yoshio Ishii *et al.*, Plenum Press, New York, 1975, p191.

(4) Kinetics of the Addition Reactions of Tetracyanoethylene to $MX(CO)L_2$(M = Rh, Ir) Type Complexes.
Masa-aki Haga, Katsuhiko Kawakami, and Toshio Tanaka,
Inorg. Chem., 15, 1946 (1976).

(5) Preparation and Stereochemistry of Rhodium-olefin Complexes containing Asymmetric Picolinaldimine Ligands.
Masa-aki Haga, Hiroshi Yukawa, and Toshio Tanaka,
J. Organometal. Chem., *in press*.

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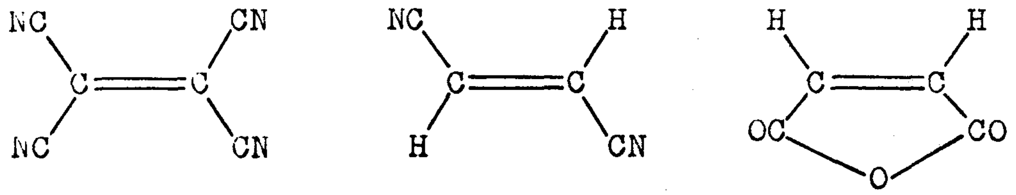
GENERAL INTRODUCTION

For the past decade, extensive developments have been attained in the field of homogeneous catalysis. Studies on the activation of small covalent molecules such as hydrogen, oxygen, nitrogen, and unsaturated organic molecules are one of the most intriguing challenges at the present time. The metal-olefin or acetylene binding process is known to play an important role in the activation of olefins or acetylenes by transition metal complexes. Recently new types of metal complexes with olefins and acetylenes have been synthesized as model compounds for the intermediates in the catalytic reactions. However, quantitative studies on such elementary processes are relatively few. For the purpose of designing highly selective and efficient catalysts it is necessary to observe the influence of the metal and the associated ligand on the binding process quantitatively.

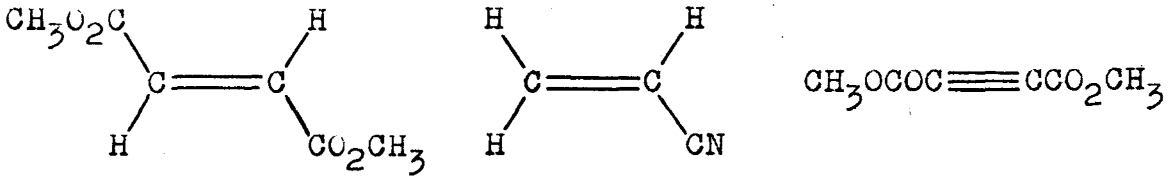
The work described in this thesis was initiated by an interest in the activation of π-bond of olefins and acetylenes by d^8 rhodium(I) and iridium(I) complexes. The specific aims are (1) the preparation of new complexes capable of activating olefins and acetylene, (2) the kinetics for the activation of olefin by a series of rhodium and iridium complexes to elucidate the role of metals, associated ligands, and solvents, and (3) the stereochemistry and stereoselectivity in the formation of metal-olefin complexes. The olefins and acetylene used in this thesis are shown in Figure 1.



tetracyanoethylene (TCNE)

fumaronitrile (FN)

maleic anhydride (MA)



dimethyl fumarate (DF)

acrylonitrile (AN)

dimethyl acetylenedicarboxylate (DAD)

Figure 1.

CHAPTER I

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

I-1. INTRODUCTION

Isocyanides are ligands with moderate σ-donor ability and intermediate in π-acceptor capacity between tertiary phosphines and carbon monoxide.[1] Very recently, renewed attention has been focused on synthesis, reactions, and structural chemistry of isocyanide complexes of rhodium(I).[2-9] However, studies on isocyanide complexes of iridium(I) are relatively sparse.[1,5,10,11]

This chapter describes the novel synthesis and characterization of tetrakis(arylisocyanide)iridium(I) and bis(arylisocyanide)tris(triphenylphosphine)iridium(I) complexes, and their reactivity to olefins and acetylene such as tetracyanoethylene(TCNE), fumaronitrile(FN), maleic anhydride(MA), dimethyl fumarate(DF), acrylonitrile(AN), and dimethyl acetylenedicarboxylate(DAD).

I-2. EXPERIMENTAL

Materials

Ammonium hexachloroiridate(IV), TCNE, and FN were commercially available, and were used as supplied. Arylisocyanides[12] and μ-dichlorodi-π-1,5-cyclooctadienediiridium(I), [Ir(COD)Cl]$_2$[13] were prepared according to literature methods.

Preparation of Complexes

(π-1,5-Cyclooctadiene)bis(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$_4$.[14] Sodium perchlorate monohydrate(2.95 g, 21 mmol) in H_2O(10 ml) was added to [Ir(COD)Cl]$_2$(1.00 g, 1.5 mmol) in CH_2Cl_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 vigorously stirred for 15 min. The CH_2Cl_2 layer was separated and washed with two portions of H_2O(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$_3$O-C$_6$H$_4$ and X = I(Ib) and PF$_6$(Ic))

p-Tolylisocyanide(0.39 g, 3.3 mmol) in CH_2Cl_2(10 ml) was added slowly to [Ir(COD)Cl]$_2$(0.30 g, 0.4 mmol) in CH_2Cl_2(10 ml) and the mixture was stirred at room temperature for 1 hr. 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_2Cl_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_4PF_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-$CH_3C_6H_4$(IIa) and p-$CH_3OC_6H_4$(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 hr, 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_2Cl_2-ether(75 %). IIb(84 %) was similarly obtained.

Oxidative Addition Reactions

Bis(p-tolylisocyanide)bis(triphenylphosphine)diiodoiridium perchlorate, $[Ir(p\text{-}CH_3C_6H_4NC)_2(PPh_3)_2I_2]ClO_4$(III)

I_2(0.052 g, 0.2 mmol) in benzene was added to IIa(0.27 g, 0.2 mmol) in CH_2Cl_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)(olefin or acetylene)iridium perchlorate, $[Ir(p\text{-}CH_3C_6H_4NC)_2(PPh_3)_2$(olefin

or acetylene)]ClO_4 (IV) (olefin or acetylene = TCNE(IVa), FN(IVb), MA(IVc), DF(IVd), AN(IVe), or DAD(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 MA.

Although compounds IVd and IVe were not isolated and characterized, CH_2Cl_2 solutions of IIa containing excess DF and AN, respectively, were investigated by means of IR and ^1H NMR spectra in order to obtain information concerning their existence in solution.

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

TABLE I COLOR AND ANALYTICAL DATA

Compound[a]	*Color*	*Analysis: Found (Calcd.)(%)*		
		C	H	N
Ia $[IrL_4]I$	Dark green	44.91 (45.13)	3.31 (3.31)	6.30 (6.57)
Ib $[IrL^*_4]I\cdot CH_2Cl_2$[b]	Dark green	45.12 (45.41)	3.59 (3.47)	6.17 (6.42)
Ic $[IrL^*_4]PF_6$	Dark green	43.76 (44.19)	3.22 (3.24)	6.62 (6.44)
IIa $[IrL_2P_3]ClO_4$	Yellow	63.31 (64.04)	4.83 (4.53)	2.23 (2.13)
IIb $[IrL^*_2P_3]ClO_4\cdot(CH_2Cl_2)_{1/2}$[b]	Yellow	61.46 (61.04)	4.46 (4.36)	2.10 (2.02)
III $[IrL_2P_2I_2]ClO_4$	Orange yellow	48.01 (47.88)	3.42 (3.40)	2.36 (2.15)
IVa $[IrL_2P_2(TCNE)]ClO_4$	White	58.56 (59.11)	3.42 (3.76)	2.36 (2.13)
IVb $[IrL_2P_2(FN)]ClO_4$	White	59.36 (59.60)	4.26 (4.11)	4.96 (4.96)
IVc $[IrL_2P_2(MA)]ClO_4$	White	58.05 (58.56)	4.05 (4.04)	2.41 (2.44)
IVf $[IrL_2P_2(DAD)]ClO_4$	White	58.16 (58.41)	4.18 (4.23)	2.49 (2.35)

[a] The abbreviations used are as follows: L = *p*-$CH_3C_6H_4NC$, L* = *p*-$CH_3OC_6H_4NC$, P = PPh_3, TCNE = tetracyanoethylene, FN = fumaronitrile, MA = maleic anhydride, and DAD = dimethyl acetylenedicarboxylate.

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

Instrumentation

Molecular weights were determined in CH_3CN at 37°C 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. ^1H NMR spectra were recorded in 2.5 to 5.0 wt% $CDCl_3$, CH_2Cl_2, or dimethylsulphoxide-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. Electronic spectra were obtained by using a 1-cm quartz cell on a Hitachi 124 spectrophotometer.

IR and ^1H NMR spectral data are given in Table II.

Table II

RELEVANT IR(cm^{-1}) AND ^1H NMR(ppm) DATA

Compound[a]	*IR*[b]		*^1H NMR*[c]		
	$\nu(N\equiv C)$	*Others*	τ(*phenyl*)	τ(CH_3 or CH_3O)	*Others*
Ia $[IrL_4]I$	2145		(3.52(broad))	(6.28(broad))	
Ib $[IrL^*_4]I\cdot CH_2Cl_2$	2153		(3.52(broad))	(7.77(broad))	
IIa $[IrL_2P_3]ClO_4$	2119(2123)		(3.00 4.13(q))	(7.79)	
IIb $[IrL^*_2P_3]ClO_4\cdot(CH_2Cl_2)_{1/2}$	2125(2126)		(3.26 4.04(q))	(6.28)	
IVa $[IrL_2P_2(TCNE)]ClO_4$	2196(2196)	$\nu(C\equiv N)$ (2226)	2.88 3.41 (q)	7.58	
IVb $[IrL_2P_2(FN)]ClO_4$	2174(2175)	$\nu(C\equiv N)$ (2216)	2.95 3.57(q)	7.60	τ(FN) 7.22
IVc $[IrL_2P_2(MA)]ClO_4$	2171(2172)		3.06 3.67(q)	7.66	τ(MA) 6.06
			2.96 3.60(q)	7.63	
IVf $[IrL_2P_2(DAD)]ClO_4$	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-$CH_3C_6H_4NC$, L* = p-$CH_3OC_6H_4NC$, TCNE = tetracyanoethylene, FN = fumaronitrile, MA = maleic anhydride, and DAD = dimethyl acetylenedicarboxylate. [b] Measured in Nujol mulls (in CH_2Cl_2). [c] Measured in $CDCl_3$(in DMSO-d_6). [d] The coupling constants of AB type quartets(q) for phenyl ring protons are all about 8 Hz.

I-3. RESULTS AND DISCUSSION

Preparation of Arylisocyanide Complexes of Iridium(I)

Although a few tetrakis(p-tolylisocyanide)iridium(I) complexes $[Ir(p\text{-}CH_3C_6H_4NC)_4]X$ (X = Br, I, and ClO_4) have been known for some time,[1] their syntheses are not necessarily simple and convenient. I have now found that reactions of a stoichiometric amount of arylisocyanides with $[Ir(COD)Cl]_2$,[13] followed by the addition of appropriate anions, easily give the desired product $[Ir(RNC)_4]X$(I) (R = $p\text{-}CH_3C_6H_4$ and X = I(Ia); R = $p\text{-}CH_3O\text{-}C_6H_4$ and X = I(Ib) and PF_6(Ic)). During the course of this investigation, a communication by McCleverty et al.[5] 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[11] reported the preparation of $[Ir(CH_3NC)_4]^+$ salts starting from $IrCl(CO)(PPh_3)_2$ and CH_3NC 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. Very recently, McCleverty et al.[10] reported in detail the isolation of $[Ir(RNC)_3(PPh_3)_2]X$ and $[Ir(RNC)_4]X$(R = t-Bu, i-Pr, $p\text{-}ClC_6H_4$, or $p\text{-}CH_3\text{-}C_6H_4$; X = Cl or PF_6).

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 go photochemical reactions, when irradiated with visible light, to show color change from dark green to orange. However, the reaction rate is drastically lower than that of the methyl isocyanide analogue,[11] 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 22,000). 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) perchlorate.[7] This fact is surprising in view of the strong tendency of low-valent transition metal complexes to undergo oxidative addition reactions.[15] 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. Conductivities of Ib in 10^{-3} and 10^{-4}M CH_3CN solutions are 67 and 97 $ohm^{-1}cm^2mol^{-1}$, respectively. Conductivity is tentatively calculated in the unit of $ohm^{-1}cm^2mol^{-1}$, 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, the conductivity 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°C 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 (ε1.2 x 10^4), which does not change much in the dark. This band, in light, gradually decreases in intensity and is finally replaced, after 15 hr, by new shoulders around 580 nm (ε 1 x 10^3) and 440 nm(ε 2 x 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 (ε 1.1 x 10^4) and 715 nm (ε 1.3 x 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.[16] 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.[16b] 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 rapidly.[11] 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).[17] Interactions between anions and cations, and between anions are well known for some square-planar complexes.[16] Very recently, it was reported that the solution oligomerization is present for $[Rh(PhNC)_4]PF_6$.[18]

Reactivity of $[Ir(p\text{-}CH_3C_6H_4NC)_2(PPh_3)_3]ClO_4$(IIa) with Various Olefins and Acetylenes

Only one strong and broad N≡C stretching band is observed for $[Ir(RNC)_2(PPh_3)_3]ClO_4$(II)(R = p-$CH_3C_6H_4$(IIa) and p-$CH_3OC_6H_4$ (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 a trigonal bipyramid with the two isocyanides in the *trans* position, in which the three phosphines are exchanging with one another to some extent. 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 $[Ir(p\text{-}CH_3C_6H_4NC)_2(PPh_3)_2I_2]ClO_4$ (III) with dissociation of one molecule of PPh_3. IIa also reacts with olefins and acetylene in CH_2Cl_2 to yield stable adducts $[Ir(p\text{-}CH_3C_6H_4NC)_2(PPh_3)_2(\text{olefin or acetylene})]ClO_4$(IV)(olefin or acetylene = TCNE(IVa), FN(IVb), MA(IVc), or DAD(IVf)), with dissociation of one molecule of PPh_3, whose configurations will be discussed later. On the other hand, reactions of IIa with DF and AN 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≡C stretching vibration and magnetic equivalence of two sets of phenyl ring protons for the isocyanide ligands(Table II) favor the configuration A in Fig. 1. IVa and IVb show little change in their ^1H NMR spectra in $CDCl_3$ in the temperature range between -30° and +55°C. This suggests that IVa and IVb have rigidly coordinated TCNE and FN, respectively. Moreover, the fact that IIa reacts even with DF and AN to some extent in solution

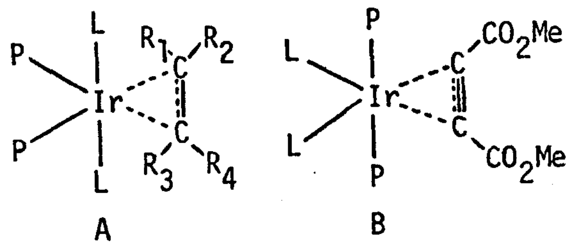


Fig. 1. Configurations of complexes.

L=p-$CH_3C_6H_4NC$, P=PPh_3
IVa: R_1=R_2=R_3=R_4=CN(TCNE)
IVb: R_1=R_4=H, R_2=R_3=CN(FN)
IVc: R_1=R_3=CO_2CO, R_2=R_4=H(MA)

indicates that the basicity of the reactive species of IIa is comparable to that of Vaska's complex, $IrCl(CO)(PPh_3)_2$.[19]

The FN complex 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.[20] 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-FN bonding in IVb contains significant σ-character.

The IR spectrum of IVc in CH_2Cl_2 shows only one N≡C stretching band(Table II), suggesting that the configuration of IVc may be also A similar to those of IVa and IVb. Another

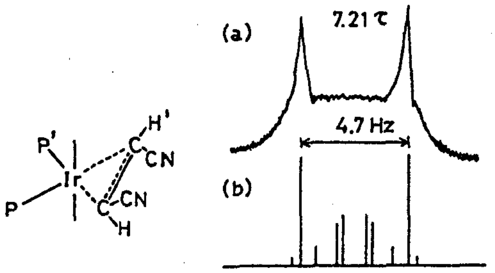


Fig. 2. The ^{1}H NMR Spectrum for the olefinic protons of [Ir(p-$CH_3C_6H_4NC)_2(PPh_3)_2$(fumaronitrile)]ClO_4. (a) The observed spectrum; (b) The calculated spectrum as an AA′XX′ system assuming ^{1}J(P–P) 1.5, ^{3}J(H–H′) 0.5, ^{3}J(P–H) 1.3, and ^{3}J(P–H′) 3.4 Hz.

proof for the configuration comes from the fact that the ^1H 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 MA. Thus, six distinct signals are observed for the phenyl ring protons of the isocyanides in the region between τ3 and 4 ppm (Table II). 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 MA appears at τ6.06 ppm(J = 3.5 Hz). Integration of the isocyanide protons and those of the coordinated MA confirms the 1 to 1 adduct formation. The coordinated MA protons of IVc show an essentially similar resonance pattern as that of the FN adduct 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 DF in the ν(N≡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 dissociation

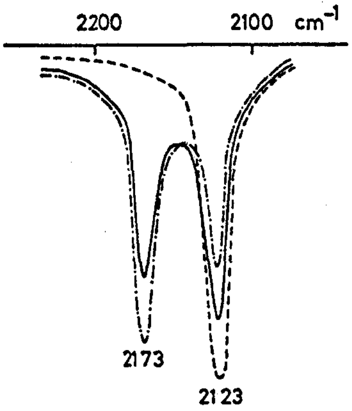


Fig. 3. The IR spectra of $[Ir(p\text{-}CH_3C_6H_4NC)_2(PPh_3)_3]ClO_4$ (IIa) with and without dimethyl fumarate (DF) in CH_2Cl_2. Molar ratio DF/IIa: 0------; 1————; 5–·–·–·–

of one molecule of PPh_3. A similar new band is observed at 2157 cm^{-1} in the case of AN. Thus, IIa is shown to form olefin complexes to some extent, even with DF and AN in solution.

A crude linear relationship is obtained between the ν(N≡C) of the olefin complexes of IIa in CH_2Cl_2 (olefin = TCNE, FN, and MA) and the electron affinity of the olefins,[21] 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 ν(CO)[22,23] of some adducts with Vaska's complex and for the ν(N≡C)[24] of some nickel and palladium isocyanide complexes.

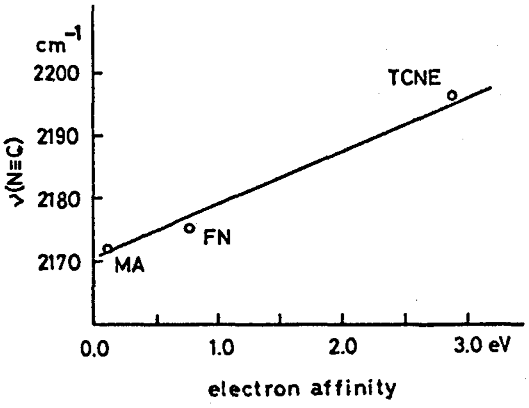


Fig. 4. A relationship between the ν(N≡C) of the olefin adducts $[Ir(p\text{-}CH_3C_6H_4NC)_2(PPh_3)_2(olefin)]ClO_4$ and the electron affinity of the olefins (TCNE = tetracyanoethylene, FN = fumaronitrile, and MA = maleic anhydride).

IIa reacts with DAD to give the white complex IVf, whose IR spectrum in CH_2Cl_2 solution shows, in a sharp contrast to those of the olefin complexes, two strong ν(N≡C) bands (Table II). This is due to the 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 B (Fig. 1). Two further bands are observed at 1772 and 1692 cm^{-1}, which are assigned to ν(C≡C) and the ester ν(C=O) bands, respectively. The ν(C≡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. 1B). May et al.[25] reported ν(C≡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 ν(C≡C) frequency of the isocyanide complex compared with that of the corresponding CO complex may be interpreted in terms of the stronger σ-donating and less π back-bonding capacity of the isocyanide ligand. It is also noteworthy that, with IIa, the olefins such as TCNE, FN, and MA, and DAD selectively form complexes of different configurations A and B in Fig. 1, respectively.

I-4. SUMMARY

Several isocyanide iridium complexes $[Ir(RNC)_4]X$(I) (R = p-$CH_3C_6H_4$, X = I; R = p-$CH_3OC_6H_4$, X = I and PF_6) and $[Ir(RNC)_2(PPh_3)_3]ClO_4$(II)(R = p-$CH_3C_6H_4$ and p-$CH_3OC_6H_4$) 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. The addition reactions of I and II with halogens, and II with olefins and acetylene such as TCNE, FN, MA, DF, AN, and DAD were described. The structures of I, II, and the olefin and acetylene complexes of II, $[Ir(p\text{-}CH_3C_6H_4NC)_2(PPh_3)_2(\text{olefin or acetylene})]ClO_4$(IV)(olefin or acetylene = TCNE, FN, MA, or DAD), are discussed on the basis of their electronic, IR, and NMR spectra. Especially, I is suggested to adopt an oligomeric structure involving Ir to Ir interaction, the result of which is relatively low reactivity in the addition reactions. Trigonal bipyramidal configurations are suggested for IV with the two isocyanides in the trans and cis positions for the olefin and acetylene complexes, respectively.

I-5. REFERENCES

1. L. Malatesta and F. Bonati, Isocyanide Complexes of Metals, Wiley, New York, 1969.
2. T. Boshi, P. Uguagliati, and B. Crociani, J. Organometal. Chem., 30, 283 (1970).
3. A. Nakamura, Y. Tatsuno, Y. Yamamoto, and S. Otsuka, J. Am. Chem. Soc., 93, 6052 (1971).
4. A. L. Balch and J. Miller, J. Organometal. Chem., 32, 263 (1971).
5. J. W. Dart, M. K. Lyoyd, J. A. McCleverty, and R. Mason, Chem. Commun., 1197 (1971).
6. R. V. Parish and P. G. Simms, J. Chem. Soc., Dalton, 809 (1972).
7. T. Kaneshima, K. Kawakami, and T. Tanaka, Inorg. Chem., 13, 2198 (1974).
8. P. R. Brason and M. Green, J. Chem. Soc., Dalton, 1303 (1972).
9. A. Nakamura, Y. Tatsuno, and S. Otsuka, Inorg. Chem., 11, 2058 (1972).

10. J. W. Dart, M. K. Lyoyd, R. Mason, and J. A. McCleverty, J. Chem. Soc., Dalton, 2039, 2046 (1972).

11. W. M. Bedford and G. Rouschias, Chem. Commun., 1224 (1972).

12. T. Shingaki and M. Takebayashi, Bull. Chem. Soc. Jpn., 36, 617 (1963).

13. G. Winkhaus and H. Singer, Chem. Ber., 99, 3610 (1966).

14. R. R. Scrock and J. A. Osborn, J. Am. Chem. Soc., 93, 2397 (1971).

15. J. P. Collman, Acc. Chem. Res., 1, 136 (1968).

16. (a) K. K. Krogmann, Angew. Chem. Intern. Edit., 8, 35 (1969); (b) S. Yamada, Kagaku(Iwanami), 41, 651 (1971).

17. C. G. Pitt, L. K. Monteith, L. F. Ballard, J. P. Collman, J. C. Morrow, W. R. Roper, and D. Ulku, J. Am. Chem. Soc., 88, 4286 (1966).

18. K. R. Mann, J. G. Gordon II, and H. B. Gray, J. Am. Chem. Soc., 97, 3553 (1975).

19. W. H. Baddley, J. Am. Chem. Soc., 90, 3705 (1968).

20. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, High Resolution Nuclear Magnetic Resonance Spectroscopy, Pergamon Press, New York, 1965, p392.

21. (a) A. C. Farragher and A. M. Page, Trans. Faraday Soc., 63, 2369 (1967); (b) C. H. Wells, Tetrahedron, 22, 1985(1966).

22. D. F. Shriver, Acc. Chem. Res., 3, 231 (1970).

23. L. Vaska, Acc. Chem. Res., 1, 335 (1968).

24. S. Otsuka, T. Yoshida, and Y. Tatsuno, J. Am. Chem. Soc., 93, 6462 (1971).

25. M. J. Church, M. J. Mays, R. N. F. Simpson, and F. P. Stefanini, J. Chem. Soc., (A), 2909 (1970).

CHAPTER II

KINETICS OF THE ADDITION REACTIONS OF TETRACYANOETHYLENE TO RHODIUM(I) AND IRIDIUM(I) COMPLEXES

II-1. INTRODUCTION

As revealed in Chapter I, olefins such as tetracyanoethylene (TCNE) react with low-valent transition metal complexes to give stable adducts. This reaction is of interest in the viewpoint of its resemblance to a fundamental step in homogeneous catalytic processes.

Kinetic and thermodynamic studies on metal-olefin interaction were performed for the reactions of trans-$IrCl(CO)(PPh_3)_2$ with trans-$CF_3(CN)C{=}C(CF_3)CN$[1] and trans-$CH_3OCOCH{=}CHCOOCH_3$[2] so far. This chapter reports the kinetics of the reactions of TCNE with several cationic isocyanide complexes of rhodium(I), $[Rh(RNC)_2L_2]ClO_4$, and with a series of $MX(CO)L_2$(M = Rh, Ir) type complexes by the stopped-flow technique.

II-2. EXPERIMENTAL

$RhCl_3 \cdot 3H_2O$ and $(NH_4)_2IrCl_6$ were of reagent grade and used as supplied. Commercial TCNE was sublimed twice. Para-substituted tertiary phosphines[3] and $P(O\text{-}\underline{o}\text{-}CH_3C_6H_4)_3$[4] were prepared by literature methods. Solvents were distilled twice, and deoxygenated by bubbling N_2 at least for 30 min before use.

Acetone was treated with an acidic $KMnO_4$ solution and then a basic $AgNO_3$ solution,[5] followed by drying over Drierite. Tetrahydrofuran(THF) was dried over lithium aluminum hydride, and benzonitrile and acetonitrile over phosphorus pentoxide.

Infrared and electronic spectra were measured as described in Chapter I.

a. $[Rh(RNC)_2L_2]^+$-TCNE system

Preparation of Starting Materials

$[Rh(\underline{p}\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2]ClO_4$ was prepared according to the literature;[6] $\nu(NC)$ 2124 cm^{-1}, $\lambda_{max}(CH_3CN)$ 419 $m\mu(\varepsilon$ 4720) and 478 $m\mu(\varepsilon$ 560). Anal. Calcd for $C_{52}H_{44}N_2O_6P_2ClRh$: C, 62.88; H, 4.46; N, 2.82. Found: C, 62.90; H, 4.38; N, 2.89. The corresponding cyclohexylisocyanide complex was similarly prepared: cyclohexylisocyanide(0.16 g, 1.5 mmol) in CH_2Cl_2 (10 ml) was added slowly to $[Rh(1,5\text{-}C_8H_{12})(PPh_3)_2]ClO_4$[7](0.60 g, 0.73 mmol) in CH_2Cl_2(10 ml). The solution was stirred under nitrogen for 30 min, during which time the color of the solution changed from orange to yellow. The solvent was removed under reduced pressure, and the resulting product was recrystallized from CH_2Cl_2-petroleum ether to give $[Rh(C_6H_{11}NC)_2(PPh_3)_2]ClO_4$(0.55 g, 80 % yield); $\nu(NC)$ 2156 cm^{-1}, $\lambda_{max}(CH_3CN)$ 401 $m\mu(\varepsilon$ 5170) and 458 $m\mu(\varepsilon$ 230). Anal. Calcd for $C_{50}H_{50}N_2O_4P_2ClRh$: C, 63.53; H, 5.54; N, 2.96. Found: C, 63.24; H, 5.45; N, 3.18.

$[Rh(\underline{p}\text{-}CH_3OC_6H_4NC)_2(P(OPh)_3)_2]ClO_4$ was similarly obtained from a reaction of $[Rh(1,5\text{-}C_8H_{12})(P(OPh)_3)_2]ClO_4$ with p-methoxyphenylisocyanide(98 % yield); ν(NC) 2154 cm^{-1}, $\lambda_{max}(CH_3CN)$ 398 mμ(ε 6310) and 455 mμ(ε 485). Anal. Calcd for $C_{52}H_{44}N_2O_{12}P_2ClRh$: C, 57.34; H, 4.07; N, 2.57. Found: C, 57.25; H, 4.16; N, 2.70.

$[Rh(p\text{-}ClC_6H_4NC)_2(PPh_3)_2]ClO_4$ was prepared as mentioned above (80 % yield); ν(NC) 2145 cm^{-1}, $\lambda_{max}(CH_3CN)$ 427 mμ(ε 3300) and 485 mμ(ε 370). Anal. Calcd for $C_{50}H_{38}N_2O_4P_2Cl_3Rh$: C, 59.93; H, 3.82; N, 2.79. Found: C, 59.63; H, 3.79; N, 2.80.

Isolation of the Addition Products

TCNE(25 mg, 0.19 mmol) was added to $[Rh(p\text{-}CH_3OC_6H_4NC)_2(P(OPh)_3)_2]ClO_4$(0.2 g, 0.18 mmol) in acetone(10 ml) at room temperature; the yellow color of the solution disappeared immediately. The solvent was evaporated under reduced pressure and the product was recrystallized from CH_2Cl_2-diethyl ether to give $[Rh(p\text{-}CH_3OC_6H_4NC)_2(P(OPh)_3)_2(TCNE)]ClO_4$(0.20 g, 91 % yield); ν(NC) 2206 cm^{-1} and ν(CN) 2232 cm^{-1}. Anal. Calcd for $C_{58}H_{44}N_6O_{12}P_2ClRh$: C, 57.23; H, 3.64; N, 6.90. Found: C, 57.16; H, 3.71; N, 7.24.

$[Rh(C_6H_{11}NC)_2(PPh_3)_2(TCNE)]ClO_4\cdot 1/2CH_2Cl_2$ was similarly obtained(90 % yield) with a half mole of dichloromethane in the crystals; ν(NC) 2212 cm^{-1} and ν(CN) of TCNE is obscured by the strong isocyanide vibration. Anal. Calcd for $C_{56.5}H_{53}N_6O_4P_2Cl_2Rh$: C, 60.82; H, 4.79; N, 7.53. Found: C, 60.43; H, 4.70; N, 7.57.

$[Rh(p\text{-}ClC_6H_4NC)_2(PPh_3)_2(TCNE)]ClO_4$ was analogously prepared (81 % yield); ν(NC) 2193 cm^{-1} and ν(CN) 2227 cm^{-1}. Anal. Calcd for $C_{56}H_{38}N_6O_4P_2Cl_3Rh$: C, 59.51; H, 3.39; N, 7.44. Found: C, 59.26; H, 3.17; N, 7.58.

Kinetic Measurements

Reaction rates were followed by measuring the transmittance in the vicinity of 400 mμ with a Union RA-1100 stopped-flow spectrophotometer and a 2 mm quartz cell. The instrument was thermostated to ± 0.2°C. The temperature at the cell was measured with a corrected thermometer. Concentrations of the complexes in solution varied between 1.2×10^{-3} and 1.0×10^{-4}M. Lambert-Beer's law was shown to be valid in the case of $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2]ClO_4$-TCNE in acetonitrile and THF, and was assumed in the other systems. All reactions were carried out under pseudo-first-order conditions, using at least a tenfold excess of TCNE. Solutions were stored in a constant temperature bath at the reaction temperature under nitrogen, and were transferred into the driving syringe of the stopped-flow apparatus. A glass syringe fitted with a 30 cm stainless steel needle was used for transferring solutions of metal complexes. Glass pipettes were used for solutions of TCNE, because the color turned yellow when a stainless steel needle was used. Solutions were allowed to stand for 15 min to ensure thermal equilibration before kinetic runs.

The changes in transmittance as a function of time were monitored by a memoryscope; a typical reaction curve is shown in Fig. 1. Five or six measurements were carried out for each run. Plots of $\ln(A_t - A_\infty)$ vs. time were found to be linear, and the pseudo-first-order rate constant, k_{obs}, was calculated by the method of least-squares, where A_t and A_∞ are absorbances at the times "t" and infinity. Rate constants were reproducible within ± 5 %.

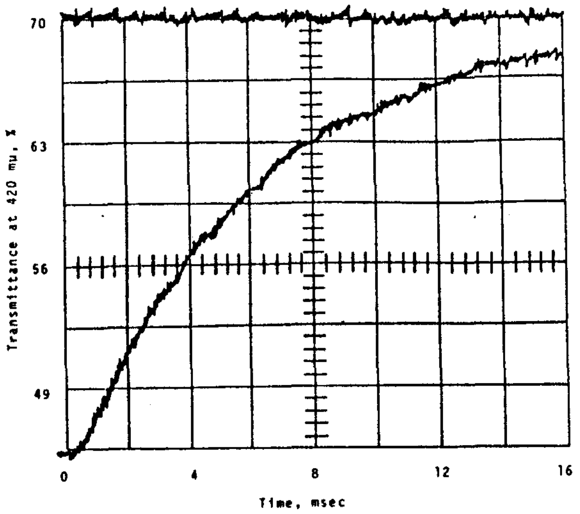


Figure 1. A typical oscillogram showing disappearance of [Rh(p-$CH_3OC_6H_4NC)_2(PPh_3)_2]ClO_4$ (monitored at 420 mμ) in reaction with TCNE in CH_3CN; [Rh] = 1.67×10^{-4} M and [TCNE] = 1.77×10^{-3} M at 35.0° C.

b. MX(CO)L_2-TCNE system

Preparation of Complexes

All experimental manipulations were performed under nitrogen. The complexes, trans-RhX(CO)L_2(X = Cl, L = P(p-$CH_3OC_6H_4)_3$, P(p-$CH_3C_6H_4)_3$, PPh_3, P(p-$ClC_6H_4)_3$, PPh_2Me, $AsPh_3$; X = Br, I, NCO, NCS, L = PPh_3), RhCl(CS)$(PPh_3)_2$, and trans-IrCl(CO)$(PPh_3)_2$, were prepared by literature methods[8] and characterized by melting points, elemental analyses, and IR spectra.

The corresponding tertiary phosphite complexes of rhodium were prepared by an improved method; ortho-tolyl phosphite(0.84 g, 2.42 mmol) in CH_2Cl_2(10 ml) was added slowly to $[Rh(C_8H_{12})Cl]_2$ (0.3 g, 0.61 mmol) in CH_2Cl_2(10 ml) at room temperature. Carbon monoxide was bubbled through the solution for about 5 min, during which time the color changed from orange to yellow. Ethanol (10 ml) was added to the solution and the solvent was partially removed under reduced pressure. The resulting precipitate was separated from the solution and recrystallized from benzene-n-hexane to give trans-RhCl(CO)(P(O-o-$CH_3C_6H_4)_3)_2$(0.74 g, 70 %), mp 130-132°C. Anal. Calcd for $C_{43}H_{42}O_7ClP_2Rh$: C, 59.29; H, 4.86. Found: C, 59.43; H, 4.73. trans-RhCl(CO)$(P(OPh)_3)_2$ was similarly prepared(90 % yield), mp 157-160°C. Anal. Calcd for $C_{37}H_{30}O_7ClP_2Rh$: C, 56.47; H, 3.84. Found: C, 56.43; H, 3.84.

Isolation and Identification of the Addition Products

TCNE(45 mg, 0.35 mmol) was added to RhCl(CO)(P(p-$CH_3OC_6H_4)_3)_2$ (0.3 g, 0.34 mmol) in benzene(30 ml) at room temperature. After being stirred for 30 min, the solution was concentrated under reduced pressure. The resulting product was recrystallized from CH_2Cl_2-n-hexane to give orange crystals of RhCl(CO)(P(p-$CH_3OC_6H_4)_3)_2$(TCNE)(0.3 g, 88 %), mp 175-180°C. Anal. Calcd for $C_{49}H_{42}N_4O_7ClP_2Rh$: C, 58.90; H, 4.23; N, 5.60. Found: C, 58.98; H, 4.01; N, 5.54. Although the addition product of RhCl(CO)L_2(L = $P(OPh)_3$, P(O-o-$CH_3C_6H_4)_3$, P(p-$CH_3C_6H_4)_3$, P(p-$ClC_6H_4)_3$) with TCNE has not been isolated, its existence in solution was ascertained by the high frequency shifts of the CO stretching band(Table I). Other 1:1 adducts were already isolated and characterized by Baddley[9] or Varshavskii et al.[10]

Table I. ν(CO) Frequencies of the Rh(I) and Ir(I) Complexes and Their TCNE Adducts, cm^{-1} [a]

Complex	Freq of complex	Freq of TCNE adduct
$RhCl(CO)(PPh_3)_2$	1975	2065
$RhCl(CO)(PPh_2Me)_2$	1972	2064
$RhCl(CO)(AsPh_3)_2$	1973	2061
$RhCl(CO)(P(OPh)_3)_2$	2013	2041
RhCl(CO)(P(O-*o*-$CH_3C_6H_4)_3)_2$	2008	2035
RhCl(CO)(P(*p*-$ClC_6H_4)_3)_2$	1982	2080
RhCl(CO)(P(*p*-$CH_3C_6H_4)_3)_2$	1972	2061
RhCl(CO)(P(*p*-$CH_3OC_6H_4)_3)_2$	1972	2057
$RhCl(CS)(PPh_3)_2$	1304[b]	1348[b]
$Rh(NCO)(CO)(PPh_3)_2$	1980	2085
$Rh(NCS)(CO)(PPh_3)_2$	1984	2080
$RhBr(CO)(PPh_3)_2$	1976	2065[c]
$RhI(CO)(PPh_3)_2$	1980	2084[c]
$IrCl(CO)(PPh_3)_2$	1965	2053

[a] In acetone. [b] ν(CS) in CH_2Cl_2. [c] These complexes showed complicated spectra, which have been assigned by comparing with those of other adducts.

Kinetic Measurements

Reaction rates were determined as described in this chapter 2a. A typical reaction curve and plots of $\ln(A_\infty - A_t)$ vs. time are shown in Figure 2.

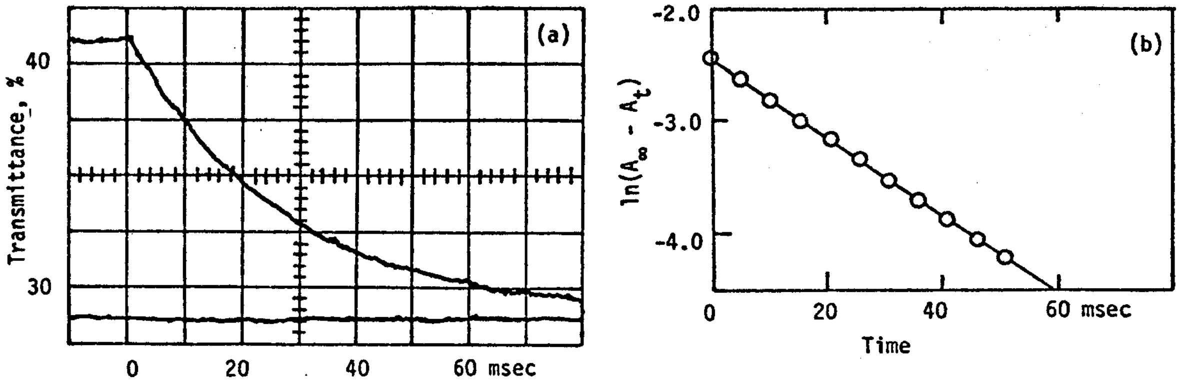


Figure 2. Transmittance changes as a function of time monitored at 430nm (a) and a plot of $\ln(A_\infty - A_t)$ against time (b) for the reaction of $RhCl(CO)(PPh_3)_2$ with TCNE in acetone at 25°C; [Rh] = 3.70×10^{-4}M, [TCNE] = 1.00×10^{-2}M.

In the interaction of TCNE with $RhCl(CO)(PPh_3)_2$ in benzonitrile and with $RhBr(CO)(PPh_3)_2$ or $RhI(CO)(PPh_3)_2$ in acetone the second reaction was observed, whose rate constants in most cases were 40-200 times smaller than those of the first reaction. The reaction of TCNE with $RhI(CO)(PPh_3)_2$ in acetone was followed between 350 and 500 nm by a Union RA-1300 stopped-flow/rapid-scan spectrophotometer. The result showed that the initial stage of the reaction was dominated by the addition reaction, followed by the formation of the TCNE anion radical, which was confirmed by the occurrence of weak characteristic hyperfine structures of the absorption in the vicinity of 420 nm: 404, 417, 425, 435, 445, 459, 470 nm(the five peaks at the shortest wavelengths were too weak to be observed; lit.[11a] 366, 374, 382, 390, 398, 407, 416, 425, 435, 445, 457, 468 nm). In addition, esr signals due to the TCNE anion radical($\langle a_N \rangle$ = 1.56 G; lit.[11b] 1.574 G) were observed in the quick mixing of TCNE with $RhCl(CO)(PPh_3)_2$ in benzonitrile at room temperature. The Guggenheim method was used to determine the rate constants for the initial reaction. In the case of $RhI(CO)(PPh_3)_2$, however, the two consecutive first-order reactions could not completely be separated, because the second reaction was as fast as the first reaction. The formation reaction of the anion radical was not further pursued, since we have been interested in the initial addition reaction.

II-3. KINETIC RESULTS

a. $[Rh(RNC)_2L_2]^+$-TCNE system

Stoichiometries of reaction 1 were established by the essentially quantitative isolation of products and by the

$$\underline{trans}\text{-}[Rh(RNC)_2L_2]ClO_4 + TCNE \longrightarrow [Rh(RNC)_2L_2(TCNE)]ClO_4 \qquad (\underline{1})$$

spectrophotometric titration of $[Rh(\underline{p}\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2]ClO_4$ with TCNE(Fig. 3). Approximate equilibrium constants ($[[Rh(\underline{p}\text{-}CH_3OC_6H_4NC)_2L_2(TCNE)]ClO_4]/[[Rh(\underline{p}\text{-}CH_3OC_6H_4NC)_2L_2]ClO_4]$-[TCNE]) were 3.3×10^4 for L = PPh_3 in 1,2-dichloroethane and 4.0×10^3 M^{-1} for L = $P(OPh)_3$ in CH_3CN(25°C).

Kinetic studies were carried out in THF, $(CH_3)_2CO$, and CH_3CN. They are good solvents for the rhodium substrates and do not react with TCNE. In the kinetic runs the reactions

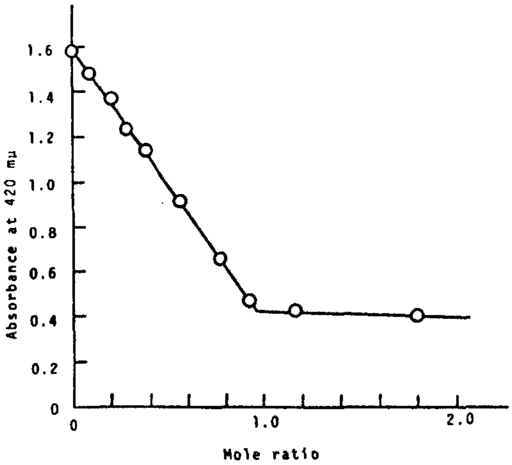


Figure 3. A plot of the absorbance at 420 mμ to the mole ratio of [TCNE]/[[Rh(p-$CH_3OC_6H_4NC$)$_2$(PPh_3)$_2$]ClO_4] in CH_2ClCH_2Cl; [Rh] = 3.38 × 10^{-4} M.

proceeded essentially to completion. The results at 25°C are given in Table II. Plots of the pseudo-first-order rate constant, k_{obs}, against [TCNE] were linear with a zero intercept; a representative one is shown in Fig. 4. This shows a simple second-order rate law:

$$-\frac{d[Rh]}{dt} = k_2[Rh][TCNE] \qquad (\underline{2})$$

Kinetic data at various temperatures are given in Table III.

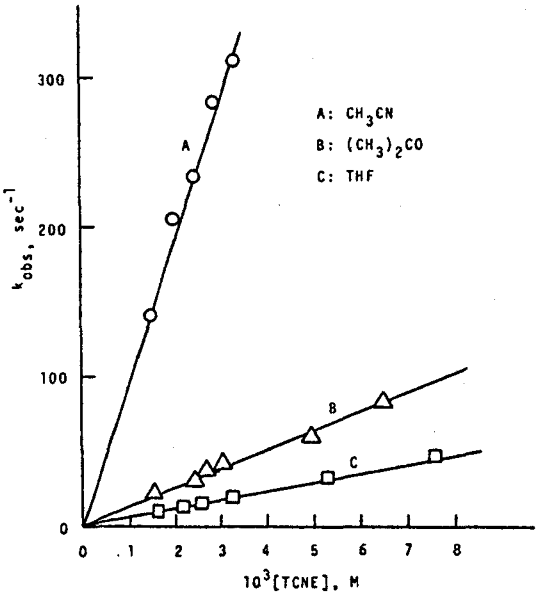


Figure 4. Second-order rate plots for the reactions of [Rh(p-$CH_3OC_6H_4NC$)$_2$(PPh_3)$_2$]ClO_4 with TCNE at 25°C, [Rh] = 1.6 × 10^{-4} M.

TABLE II. Rates of Reactions of $[Rh(RNC)_2L_2]ClO_4$ with TCNE at 25° C. Effects of Variation in Solvent and Ligand.

Solvent	10^3[TCNE] *M*	k_{obs} sec^{-1}	$10^{-4}k_2$ M^{-1} sec^{-1}
R = *p*-$CH_3OC_6H_4$. L = PPh_3			
CH_3CN	1.57	140	8.92
	2.04	197	9.67
	2.57	234	9.11
	2.98	284	9.53
	3.47	310	8.94
$(CH_3)_2CO$	1.65	23.1	1.40
	2.48	34.4	1.39
	2.78	40.3	1.45
	3.04	42.1	1.38
	5.00	60.8	1.22
	6.50	85.8	1.32
THF	1.68	10.2	0.61[a]
	2.25	13.3	0.59
	2.69	15.6	0.58
	3.30	18.8	0.57[b]
	5.37	31.7	0.59
	7.65	46.7	0.61
R = *p*-$CH_3OC_6H_4$, L = $P(OPh)_3$			
CH_3CN	1.48	134	9.05
	1.90	178	9.37
	2.12	201	9.48
	2.64	232	8.79
$(CH_3)_2CO$	1.61	37.9	2.35
	2.13	60.2	2.83
	2.94	71.3	2.43
THF	1.64	23.9	1.46
	2.14	33.2	1.55
	2.63	37.8	1.44
	2.82	40.6	1.44
	3.33	47.6	1.43
R = *cyclo*-C_6H_{11}, L = PPh_3			
CH_3CN	1.50	459	30.6
	1.70	450	26.5
	2.04	598	29.3
	2.31	777	33.6
R = *p*-ClC_6H_4, L = PPh_3			
CH_3CN	2.20	51.4	2.34
	2.72	62.8	2.31
	3.20	83.6	2.61
	4.44	94.2	2.12

[a] The influence of the addition of sodium perchlorate to the reactants on the reaction rate was investigated: $[NaClO_4] = 1.64 \times 10^{-2} M$, $k_2 = 0.58 \times 10^4$ M^{-1} sec^{-1}; $[NaClO_4] = 8.31 \times 10^{-2} M$, $k_2 = 0.53 \times 10^4$ M^{-1} sec^{-1}. [b] k_2 at 25° C in changing the counter anion ClO_4^- into PF_6^-: 0.45×10^4 M^{-1} sec^{-1}.

TABLE III. Second-order Rate Constants for the Reactions of $[Rh(RNC)_2L_2]ClO_4$ with TCNE at Various Temperatures.

Solvent	T (° C)	10^{-4} k_2 M^{-1} sec^{-1}
R = *p*-$CH_3OC_6H_4$, L = PPh_3		
CH_3CN	5.0	6.32 ± 0.35
	15.0	7.61 ± 0.30
	25.0	9.23 ± 0.34
	35.0	10.4 ± 0.1
$(CH_3)_2CO$	5.0	0.83 ± 0.02
	15.0	1.11 ± 0.01
	25.0	1.36 ± 0.08
	35.0	1.71 ± 0.04
THF	5.0	0.22 ± 0.01
	15.0	0.39 ± 0.02
	25.0	0.59 ± 0.01
	35.0	0.94 ± 0.01
R = *p*-$CH_3OC_6H_4$, L = $P(OPh)_3$		
CH_3CN	5.0	5.18 ± 0.02
	15.0	6.96 ± 0.06
	25.0	9.17 ± 0.30
	35.0	11.9 ± 0.2

Table IV. Activation Parameters for Reactions of $[Rh(p\text{-}CH_3OC_6H_4NC)_2L_2]ClO_4$ with TCNE.

L	Solvent	ΔH^* Kcal mol^{-1}	ΔS^* e.u.
PPh_3	CH_3CN	2.2 ± 0.1	−28.3 ± 3.2
PPh_3	$(CH_3)_2CO$	3.5 ± 0.2	−27.7 ± 3.4
PPh_3	THF	7.6 ± 0.2	−15.2 ± 2.2
$P(OPh)_3$	CH_3CN	4.1 ± 0.1	−22.0 ± 2.5

The reaction of $[Rh(\underline{p}-CH_3OC_6H_4NC)_2L_2]ClO_4$(L = PPh_3 or $P(OPh)_3$) has a large solvent effect; the reaction becomes faster in the order of THF $<$ $(CH_3)_2CO$ $<$ CH_3CN, which is consistent with increasing solvent polarity. Similar solvent effects were reported for the reactions of methyl iodide with π-$C_5H_5M(CO)L$ (where M = Co, Rh, and Ir)[12] and with trans-$IrCl(CO)(PPh_3)_2$.[13] The present complexes are ionic and it may be possible that they exist as ion pairs in media of low dielectric constant. Ion pairing alone, however, cannot account for the observed solvent effects. The addition of sodium perchlorate, up to 500 times the concentration of complex in THF, or changing the counter ion from ClO_4^- to PF_6^- has only a slight effect on the rate. In addition, good second-order kinetics were observed in each solvent for the reaction of $[Rh(\underline{p}-CH_3OC_6H_4NC)_2(PPh_3)_2]ClO_4$.

Plots of ln k_2 vs. 1/T(°K) give a straight line, from which activation parameters(Table IV) were calculated using the Eyring equation. They also show a strong solvent dependence. ΔH^* and ΔS^* decrease in the order of THF $\gg$ $(CH_3)_2CO$ $\geq$ CH_3CN. Although the ΔH^* values in $(CH_3)_2CO$ and CH_3CN are small, they are similar to values reported for reactions of this kind.[14, 15]

Changing the isocyanide ligands in $[Rh(RNC)_2(PPh_3)_2]ClO_4$ increases the rate in the order of $\underline{p}$-ClC_6H_4 $<$ $\underline{p}$-$CH_3OC_6H_4$ $<$ cyclo-C_6H_{11}, as expected for increasing electron density on the metal. On the other hand, the substitution of triphenylphosphite for triphenylphosphine in $[Rh(\underline{p}-CH_3OC_6H_4NC)_2(PPh_3)_2]$-$ClO_4$ causes little change in reaction rate. This cannot be interpreted as an electronic effect only, since ν(NC) is lower in the PPh_3 complex. Recently it was suggested that ν(CO) in Vaska's type complexes is related to their reactivity.[16] It is safe to assume that a similar relation holds for our isocyanide complexes. I interpret the similar rates on replacing PPh_3 with $P(OPh)_3$ as a near cancellation of steric and electronic effects. Larger steric hindrance to TCNE approach is expected for PPh_3 because of its larger cone angle.[17]

b. $MX(CO)L_2$-TCNE system

Kinetics

Electronic spectra of $RhCl(CO)(PPh_3)_2$ in acetone with varying amounts of TCNE are shown in Fig. 5.

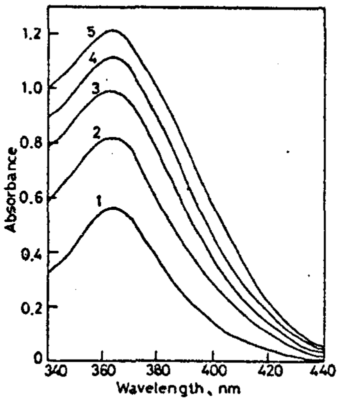


Figure 5. Electronic spectra of $RhCl(CO)(PPh_3)_2$ (1.98×10^{-4} M) in acetone with varying amounts of TCNE: (1) 0, (2) 4.25×10^{-4} M, (3) 8.50×10^{-4} M, (4) 1.27×10^{-3} M, (5) 2.12×10^{-3} M.

A similar equilibrium was found in the systems of $RhCl(CO)L_2$-TCNE (L = $P(\underline{p}\text{-}CH_3OC_6H_4)_3$ or $P(\underline{p}\text{-}CH_3C_6H_4)_3$). Thus, the reaction of trans-$MX(CO)L_2$ with TCNE is considered to be reversible(eq. 3).

$$\underline{\text{trans}}\text{-}MX(CO)L_2 + TCNE \rightleftharpoons [(TCNE)MX(CO)L_2] \qquad (3)$$

Plots of the observed rate constants(k_{obs}) vs. the concentration of TCNE gave straight lines with nonzero intercepts; a representative result for the reaction of $RhCl(CO)(PPh_3)_2$ with TCNE at various temperatures is depicted in Fig. 6.

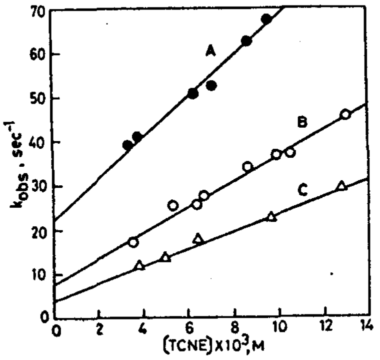


Figure 6. Plots of k_{obs} vs. [TCNE] for the reactions of $RhCl(CO)(PPh_3)_2$ (3.1×10^{-4} M) with TCNE in acetone at different temperatures: A, 34.5 °C; B 25.0 °C; C, 15.5 °C.

The addition of free triphenylphosphine in the reaction of $RhCl(CO)(PPh_3)_2$ with TCNE, up to 100 times the concentration of the complex in acetone, has little effect on the rate in the low TCNE concentration range. Therefore, it is considered that the dissociation of the phosphine may not participate in the reaction. However, for the high TCNE concentrations($> 8.4 \times 10^{-3}$ M) the reaction was dominated by the fast reaction between TCNE and free triphenylphosphine.[18] For the reversible reaction of the eq. 3 the rate law can be written:

$$-\frac{d[MX(CO)L_2]}{dt} = k_2[MX(CO)L_2][TCNE] - k_{-1}[(TCNE)MX(CO)L_2] \quad (4)$$

where k_2 and k_{-1} are the forward second-order and the backward first-order rate constants, respectively. In the presence of a large excess of TCNE, the observed rate constants k_{obs} are written as follows:[19]

$$k_{obs} = k_2[TCNE] + k_{-1} \quad (5)$$

Table V lists the k_2 and k_{-1} values obtained from the slope

Table V.

Values of k_2, k_{-1}, and K for the Reaction of $MX(CO)L_2$ with TCNE in Acetone

Compd	Temp, °C	$10^{-3}k_2$, $M^{-1}\ s^{-1}$	k_{-1}, s^{-1}	K $(=k_2/k_{-1})$, M^{-1}
$RhCl(CO)(PPh_3)_2$	15.5	1.97 ± 0.05	3.88 ± 0.44	508 ± 59
$RhCl(CO)(PPh_3)_2$	25.0	2.89 ± 0.10	7.86 ± 0.86	370 ± 43 (330 ± 40)[c]
$RhCl(CO)(PPh_3)_2$[a]	25.0	1.36 ± 0.12	23.3 ± 0.8	58 ± 5
$RhCl(CO)(PPh_3)_2$[b]	25.0	7.44 ± 0.30	3.57 ± 1.31	2 000 ± 700
$RhCl(CO)(PPh_3)_2$	34.5	4.48 ± 0.22	22.8 ± 1.52	196 ± 16
$RhBr(CO)(PPh_3)_2$	25.0	0.88 ± 0.08	15.8 ± 0.6	56 ± 5
$Rh(NCS)(CO)(PPh_3)_2$	25.0	0.81 ± 0.05	8.19 ± 0.39	99 ± 7
$Rh(NCO)(CO)(PPh_3)_2$	25.0	2.98 ± 0.10	5.27 ± 0.81	560 ± 90
$RhCl(CO)(AsPh_3)_2$	25.0	146 ± 14[d]		
$RhCl(CO)(P(p\text{-}CH_3OC_6H_4)_3)_2$	25.0	27.7 ± 1.3	(2.11 ± 0.22)[e]	(13 100 ± 1400)[c]
$RhCl(CO)(P(p\text{-}CH_3C_6H_4)_3)_2$	25.0	11.4 ± 0.2	(3.48 ± 0.39)[e]	3 280 ± 400)[c]
$RhCl(CO)(P(p\text{-}ClC_6H_4)_3)_2$	25.0	1.66 ± 0.17	23.9 ± 2.9	69 ± 10
$RhCl(CO)(P(OPh)_3)_2$	25.0	9.37 ± 0.66	81.4 ± 6.6	115 ± 12
$RhCl(CO)(P(O\text{-}o\text{-}CH_3C_6H_4)_3)_2$	25.0	0.92 ± 0.01	26.7 ± 2.3	34 ± 4
$RhCl(CS)(PPh_3)_2$	25.0	3.01 ± 0.12	6.20 ± 0.77	480 ± 62
$IrCl(CO)(PPh_3)_2$	15.2	22.5 ± 0.8[d]		
$IrCl(CO)(PPh_3)_2$	25.0	25.2 ± 0.8[d]		
$IrCl(CO)(PPh_3)_2$[a]	25.0	12.2 ± 0.6[d]		(140 000)[f]
$IrCl(CO)(PPh_3)_2$	35.0	28.0 ± 0.3[d]		

[a] In THF. [b] In C_6H_5CN. [c] Obtained spectrophotometrically by the method of N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, 81, 6138 (1959). [d] Obtained by neglecting k_{-1}, which is too small. [e] Calculated from $k_{-1} = k_2/K$. [f] In THF at 30 °C; ref 29.

and intercept of the linear relationship between k_{obs} and [TCNE]. For the reaction of $RhCl(CO)(PPh_3)_2$ with TCNE in acetone the equilibrium constant evaluated from the kinetic results(as $K = k_2/k_{-1}$) is consistent with that obtained by the spectrophotometric method(see Table V). Table V also contains rate data at various temperatures for the two representative reactions of $RhCl(CO)(PPh_3)_2$ and $IrCl(CO)(PPh_3)_2$ with TCNE in acetone. The plots of log k_2, log k_{-1}, or log K vs. 1/T(°K) gave straight lines, from which the activation parameters or thermodynamic parameters were calculated(Table VI).

Table VI. Activation Parameters for the Reaction of the Metal Substrates with TCNE in Acetone at 25 °C

Compd	ΔH_2^*,[a] kcal/mol	ΔS_2^*,[a] eu
$RhCl(CO)(PPh_3)_2$[b]	7.0 ± 0.3	−19.4 ± 1.0
$[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2]^+$[c]	3.5 ± 0.2	−27.7 ± 3.4
$IrCl(CO)(PPh_3)_2$	1.4 ± 0.1	−33.8 ± 0.1

[a] The subscript 2 stands for the forward reaction. [b] $\Delta H_{-1}^* = 15.8 \pm 1.5$ kcal/mol; $\Delta S_{-1}^* = -1.4 \pm 3.0$ eu; $\Delta H^\circ = -8.8 \pm 1.0$ kcal/mol; $\Delta S^\circ = -18.0 \pm 3.0$ eu; subscript −1 stands for the reverse reaction. [c] $k_2 = 1.36 \times 10^4\ M^{-1}\ s^{-1}$

Dependence on Ligands, Metals, and Solvents

The rate constant k_2 in the reaction of trans-$RhX(CO)(PPh_3)_2$ with TCNE increases in the order X = $NCS \simeq Br < Cl \simeq NCO$. On the other hand, in the $RhCl(CO)L_2$ complex k_2 increases in the order L = $P(O\text{-}o\text{-}CH_3C_6H_4)_3 < P(p\text{-}ClC_6H_4)_3 < PPh_3 < P(OPh)_3 < P(p\text{-}CH_3C_6H_4)_3 < P(p\text{-}CH_3OC_6H_4)_3 < AsPh_3 \ll PPh_2Me$(too fast to measure). By plotting log k_2 against the Hammett σ_p constants of the para substituents, a straight line with the slope $\rho = -2.5$ is obtained. This negative ρ value indicates that the reaction is accelerated by electron-releasing substituents, which increase the nucleophilicity of the metal substrate.

The difference in the reaction rate between $RhCl(CO)(PPh_3)_2$ and $RhCl(CS)(PPh_3)_2$ is very small, but $IrCl(CO)(PPh_3)_2$ reacts with TCNE about nine times faster than $RhCl(CO)(PPh_3)_2$ in acetone at 25°C(Table V).

The reaction rate are strongly dependent on the solvent; k_2 of the reaction between $MCl(CO)(PPh_3)_2$(M = Rh, Ir) and TCNE increases in the order THF $< (CH_3)_2CO < C_6H_5CN$, and k_{-1} varies inversely(Table V). In addition, the K value in the Rh(I) complex undergoes the larger solvent effect than k_2. The final product is therefore suggested to be more polar than the activated complex.

II-4. DISCUSSION ——— MECHANISTIC CONSIDERATION

The entropies of activation ΔS_2^* for the reaction of trans-$MCl(CO)(PPh_3)_2$(M = Rh, Ir) with TCNE are large negative values

(Table VI), which indicate that the reaction undergoes stereochemical restrictions in the transition state. Furthermore, the negative ρ value indicates the reaction occurs <u>via</u> the nucleophilic attack of the metal complexes toward TCNE. The metal complex may be possible to interact with TCNE at three different sites;[20] (1) the carbon-carbon double bond, (2) the carbon-nitrogen triple bond, and (3) the nitrile nitrogen[21](Fig. 7). In view of the low oxidation state of Rh(I) and Ir(I),

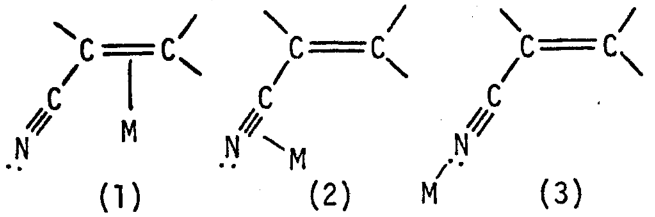
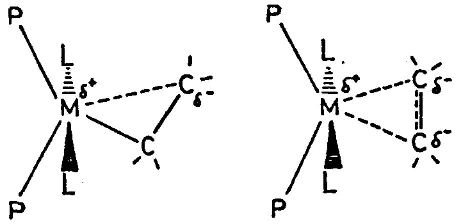


Figure 7. Possible modes of bonding of TCNE to metal complexes.

the present metal complexes are likely to prefer soft-soft interaction with TCNE.[22] Thus, site (1) or (2) is more favorable than site (3). No rhodium and iridium complexes of TCNE with the bonding mode of site (2), however, are known up to the present. Thus, the C≡N bond is less likely to be the reaction site.

In the case of the reaction site being the C=C bond, there are two possible mechanisms in the nucleophilic attack; (1a) an asymmetric interaction in a nonconcerted fashion and (1b) a symmetric coordination in a concerted manner. In both proposed transition states(1a and 1b) a dipole is induced by a prerequisite deformation of the square planar complex[23] and the electron transfer from the metal complex to TCNE. This is consistent with a large solvent effect on the reaction rate



(1a) (1b)

P=phosphorus or arsenic ligand
L=RNC, CO, or anionic ligand

and the activation parameters.

In the reactions of TCNE to $[Rh(RNC)_2L_2]^+$, the solvent molecules in a polar solvent may be strongly oriented surrounding the cationic complex, and the induced charge separation will cause stronger orientation of the solvent molecules for the activated complex than for the reactants. Thus, a negative ΔS_2^* and a small ΔH_2^* are observed in a polar solvent as the dipolar activated complex is stabilized by solvation(Table IV).

In the reactions of TCNE to trans-$RhX(CO)(PPh_3)_2$ the appearance of TCNE anion radical is remarkably dependent on the nature of halide ligands. $RhCl(CO)(PPh_3)_2$ forms the radical only in a very polar solvent benzonitrile, while the bromo and iodo analogs produce it even in acetone. In view of the fact that bromide and iodide are more polarizable than chloride,[24] the appearance of the anion radical seems to suggest a complete charge separation induced on the asymmetric dipolar intermediate in the mechanism 1a. However, the radical formation might be a side reaction.[25] Consequently, the present results will equally be interpreted by either of the transition states 1a or 1b. On the other hand, it was recently reported that the reaction of cis/trans-$CF_3(CN)C{=}C(CF_3)CN$ with $IrCl(CO)(PPh_3)_2$ gave only [(trans-$CF_3(CN)C{=}C(CF_3)CN)\cdot IrCl(CO)(PPh_3)_2$] and this was interpreted in terms of the transition state <u>1a</u>.[1]

Figure 8 shows the LFER plots[26] of log k_2 vs. log K and log k_{-1} vs. log K for a series of reactions of $RhCl(CO)L_2$ (L = phosphorus ligands) with TCNE. The linear relations except for $P(OPh)_3$[27] are indicative of a single mechanism for these reactions. It has previously been proposed that a value of β(the slope of the plot) near zero or unity implies the structure of an activated complex resembling that of the reactant or of the product.[28] The LFER plots gave the values of $\beta_2 = 0.55$(for log k_2 vs. log K) and $\beta_{-1} = -0.45$(for log k_{-1} vs. log K). Therefore, in the transition state the configuration around the rhodium would be in the middle of those of the reactant and product. Thus, in the activated complex the two trans-phosphorus or -arsenic ligands may be moderately bent back and considerable electron transfer from the metal to TCNE may take place.

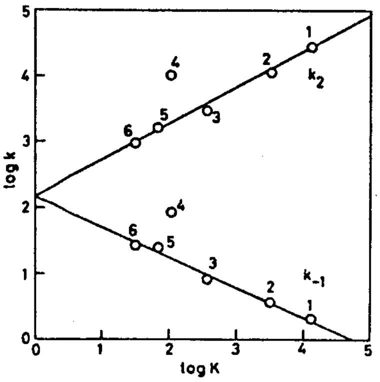


Figure 8. Linear free energy relationships for the reversible reaction $RhCl(CO)L_2 + TCNE \rightleftharpoons [(TCNE)RhCl(CO)L_2]$ in acetone at 25 °C; L = $P(p\text{-}CH_3OC_6H_4)_3$ (1), $P(p\text{-}CH_3C_6H_4)_3$ (2), PPh_3 (3), $P(OPh)_3$ (4), $P(p\text{-}ClC_6H_4)_3$ (5), $P(O\text{-}o\text{-}CH_3C_6H_4)_3$ (6).

Finally, it can be concluded from the ΔH_2^* values and the k_2 values at 25°C(Table V and VI) that the nucleophilicity of the metal substrate increases in the order of $RhCl(CO)(PPh_3)_2 < [Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2]^+ < IrCl(CO)(PPh_3)_2$.

II-5. SUMMARY

The kinetics of the addition reactions of tetracyanoethylene (TCNE) to trans-$[Rh(RNC)_2L_2]ClO_4$, where R = p-$CH_3OC_6H_4$, p-ClC_6H_4, and C_6H_{11} and L = PPh_3 and $P(OPh)_3$, in acetonitrile, acetone, and tetrahydrofuran(THF) have been investigated employing stopped-flow technique. The reaction is first order with respect to both complex and TCNE. The reaction rate increases with increasing solvent polarity in the order of THF $<$ acetone $<$ acetonitrile. The activation parameters for the reactions of $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2]ClO_4$ in the three solvents were: ΔH^*, 7.6, 3.5, 2.2 kcal mol^{-1}; ΔS^*, -15.2, -27.7, -28.3 eu.

Subsequently, the kinetics of the reactions of TCNE to the complexes, trans-$RhX(CO)L_2$(X = Cl, L = $P(p\text{-}CH_3OC_6H_4)_3$, $P(p\text{-}CH_3\text{-}C_6H_4)_3$, PPh_3, $P(p\text{-}ClC_6H_4)_3$, PPh_2Me, $AsPh_3$, $P(O\text{-}o\text{-}CH_3C_6H_4)_3$, $P(OPh)_3$; X = Br, I, NCO, NCS, L = PPh_3), $RhCl(CS)(PPh_3)_2$, and trans-$IrCl(CO)(PPh_3)_2$ were investigated. The kinetics were found to obey the rate law for a reversible reaction, $-d[MX(CO)L_2]/dt = k_2[MX(CO)L_2][TCNE] - k_{-1}[(TCNE)MX(CO)L_2]$, where k_2 and k_{-1} are the forward second-order and the backward first-order rate constants, respectively. The rate constant k_2 increases in the following orders of the anionic ligand X for trans-$RhX(CO)(PPh_3)_2$ and of the neutral ligand L for trans-$RhCl(CO)L_2$ respectively: X = NCS $\simeq$ Br $<$ Cl $\simeq$ NCO and L = $P(O\text{-}o\text{-}CH_3C_6H_4)_3 < P(p\text{-}ClC_6H_4)_3 < PPh_3 < P(OPh)_3 < P(p\text{-}CH_3C_6H_4)_3 < P(p\text{-}CH_3O\text{-}C_6H_4)_3 < AsPh_3 \ll PPh_2Me$. $IrCl(CO)(PPh_3)_2$ reacts with TCNE about nine times faster than $RhCl(CO)(PPh_3)_2$ in acetone at 25°C. The k_2 value also increases with increasing solvent polarity.

Plots of log k_2 and log k_{-1} against log $K(= k_2/k_{-1})$ give straight lines with slopes of 0.55 and -0.45 respectively. In addition, the formation of the TCNE anion radical was observed in some reactions in benzonitrile or acetone.

From these two kinetic results, it is concluded that the reaction involves a dipolar activated complex formed by the nucleophilic attack of the metal complex on TCNE.

II-6. REFERENCES AND NOTES

1. J. Ashley-Smith, M. Green, and D. C. Wood, J. Chem. Soc. (A), 1847 (1970).
2. W. Strohmeier and R. Fleischmann, Z. Naturforsch., B, 24, 1217 (1969).
3. F. G. Mann and E. J. Chaplin, J. Chem. Soc., 527 (1937).
4. E. N. Walsh, J. Am. Chem. Soc., 81, 3023 (1959).
5. R. F. Hudson and J. E. Wardill, J. Chem. Soc., 1731 (1950).
6. L. Vallarino, Gazz. Chim. Ital., 89, 1632 (1959).
7. R. R. Schrock and J. A. Osborn, J. Am. Chem. Soc., 93, 2397 (1971).
8. (a) D. Evans, J. A. Osborn, and G. Wilkinson, Inorg. Synth., 11, 99 (1968); (b) M. A. Jennings and A. Wojcicki, Inorg. Chem., 6, 1854 (1967); (c) M. C. Baird and G. Wilkinson, Chem. Commun., 267 (1966); (d) L. Vallarino, J. Chem. Soc., 2473 (1957); (e) K. Vrieze, Inorg. Synth., 11, 101 (1968).
9. W. H. Baddley, J. Am. Chem. Soc., 88, 4545 (1966).
10. Y. S. Varshavskii, T. G. Cherkasova, M. M. Singh, and N.

A. Buzina, Russ. J. Inorg. Chem.(Engl. Transl.), 15, 1427 (1970).

11. (a) O. W. Webster, W. Mahler, and R. E. Benson, J. Am. Chem. Soc., 84, 3678 (1962); (b) P. H. Reiger, I. Bernal, and G. K. Fraenkel, ibid., 83, 3918 (1961).

12. A. J. Hart-Davis and W. A. G. Graham, Inorg. Chem., 9, 2658 (1970).

13. H. Stieger and H. Kelm, J. Phys. Chem., 77, 290 (1973).

14. V. J. Choy and C. J. O'Connor, J. Chem. Soc., Dalton, 2017 (1972).

15. L. Vaska, L. S. Chen, and W. V. Miller, J. Am. Chem. Soc., 93, 6671 (1971).

16. L. Vaska and L. S. Chen, Chem. Commun., 1080 (1971).

17. (a) C. A. Tolman, J. Am. Chem. Soc., 92, 2956 (1970); (b) C. A. Tolman, W. C. Seidel, and L. W. Gosser, ibid., 96, 53 (1974).

18. G. S. Reddy and C. D. Weis, J. Org. Chem., 28, 1822 (1963).

19. A. A. Frost and R. G. Pearson, Kinetics and Mechanism, 2d ed, Wiley, New York, N. Y., 1961, p186.

20. W. H. Baddley, Inorg. Chim. Acta. Rev., 2, 5 (1968).

21. M. F. Rettig and R. M. Wing, Inorg. Chem., 8, 2685 (1969).

22. R. G. Pearson, J. Am. Chem. Soc., 85, 3533 (1963).

23. J. F. Harrod and C. A. Smith, J. Am. Chem. Soc., 92, 2699 (1970).

24. C. K. Jorgensen, Coord. Chem. Rev., 1, 164 (1966).

25. N. Kushibiki and H. Yoshida, J. Am. Chem. Soc., 98, 268 (1976).

26. L. Vaska and M. F. Werneke, Trans. N. Y. Acad. Sci., 33,

27. There are marked deviations from the linear relationships in the $P(OPh)_3$ complex. The Tolman's cone angle for $P(OPh)_3$ is 128°, whereas those for $P(\underline{p}\text{-}XC_6H_4)_3$($X = CH_3O$, CH_3, H, and Cl) and $P(O\text{-}\underline{o}\text{-}CH_3C_6H_4)_3$ are 145° and 141° respectively;[17] the steric release for the $P(OPh)_3$ complex is considered to reflect the deviations. Thus, the reaction is suggested to involve different mechanistic details which presumably arise from steric effect.

28. J. E. Leffler and E. Grunwald, Rates and Equilibria of Organic Reactions, Wiley, New York, N. Y., 1963, p128.

29. L. Vaska, Acc. Chem. Res., 1, 335 (1968).

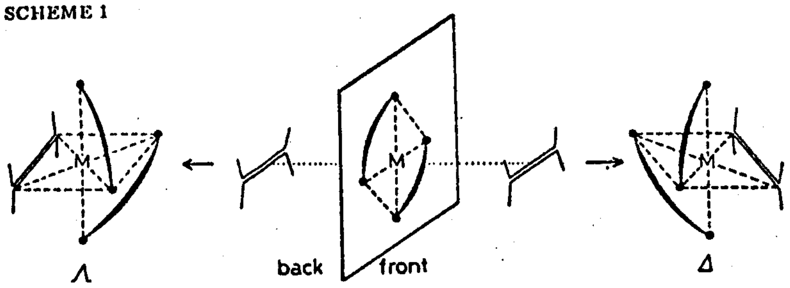
CHAPTER III

PREPARATION AND STEREOCHEMISTRY OF RHODIUM-OLEFIN COMPLEXES CONTAINING ASYMMETRIC PICOLINALDIMINE

III-1. INTRODUCTION

Asymmetric homogeneous catalytic reactions by chiral transition metal complexes, such as hydrogenation of prochiral olefins and ketones, have recently been studied by a number of workers.[1] Chiral ligands play a key role in these asymmetric reactions. The author attempted to prepare stable chiral olefin-rhodium complexes, which may be useful model compounds to help understand the mechanism of enantioselective reactions.[2] A nitrogen chelate with chirality was chosen, N-(S)-phenylethylpicolinaldimine,[3] $2\text{-}C_5H_4NCH\text{=}N\text{-}(S)\text{-}CHMePh$. When an olefin or an acetylene oxidatively adds to a bis-chelated rhodium complex, the metal center is converted into a chiral moiety(Scheme 1).

SCHEME 1



In addition, a pair of diastereomeric complexes is formed when a chiral chelate or a prochiral olefin is used.[4] The extent of stereoselectivity in asymmetric rhodium catalysts may be affected by the chiralities both of the metal center and of the coordinated olefin.

This chapter describes the preparation and stereochemistry of the complexes $[Rh(2\text{-}C_5H_4NCH{=}N\text{-}R)_2]ClO_4$(R = (S)-CHMePh, CH_2Ph, tert-Bu) and their adducts with an olefin or an acetylene.

III-2. EXPERIMENTAL

Materials and General Procedures

α-Phenylethylamine was resolved using (+)-tartaric acid[5] to give the S(-)-enantiomorph, $[\alpha]_D^{24}$ -38.6°(neat)(lit.[6], $[\alpha]_D^{22}$ -40.3°). N-Alkylpicolinaldimines were prepared according to the literature.[3] An ethanol solution of (S)-α-phenylethylamine and 2-picolinaldehyde was refluxed for about 3 hr, followed by distillation to give N-(S)-α-phenylethylpicolinaldimine; b.p. 141°C/3 mmHg, $[\alpha]_D^{24}$ +42.2°(c 5.86, CH_3OH). $[Rh(C_2H_4)_2Cl]_2$ was prepared by the literature method.[7]

Preparation of the complexes was carried out at room temperature under nitrogen. Solvents were degassed before use.

Bis(N-substituted picolinaldimine)rhodium perchlorate, $[Rh(2\text{-}C_5H_4NCH{=}N\text{-}R)_2]ClO_4$(R = (S)-CHMePh(I), CH_2Ph(II), tert-Bu(III)).

A methanol solution(10 ml) of $2\text{-}C_5H_4NCH{=}N$-(S)-CHMePh(0.36 g, 1.7 mmol) was added slowly to a suspension of $[Rh(C_2H_4)_2Cl]_2$ (0.16 g, 0.4 mmol) in methanol(15 ml) to evolve ethylene immediately. The clear solution obtained was stirred for 1 hr, during which time the color of the solution changed from orange to violet. Addition of $NaClO_4 \cdot H_2O$(0.2 g, 1.4 mmol) in methanol (5 ml) to the solution yielded violet microcrystals of **I**, which were filtered, washed with methanol three times, and dried *in vacuo*, yielding 0.40 g(80 %); Λ_M = 153 $ohm^{-1}cm^2mol^{-1}$. *Anal*. Calcd for $C_{28}H_{28}N_4O_4ClRh$: C, 53.99; H, 4.53; N, 8.99 %. Found: C, 54.00; H, 4.79; N, 8.63 %.

II and **III** were similarly prepared by using the appropriate picolinaldimine(75 and 70 % respectively); the former was solvated with one molecule of methanol. **II**: Λ_M = 143 $ohm^{-1}cm^2mol^{-1}$. *Anal*. Calcd for $C_{26}H_{24}N_4O_4ClRh \cdot CH_3OH$: C, 51.73; H, 4.50; N, 8.94 %. Found: C, 51.14; H, 4.19; N, 8.73 %. **III**: Λ_M = 142 $ohm^{-1}cm^2mol^{-1}$. *Anal*. Calcd for $C_{20}H_{28}N_4O_4ClRh$: C, 45.60; H, 5.36; N, 10.63 %. Found: C, 45.80; H, 5.48; N, 9.93 %.

Bis[N-(S)-α-phenylethylpicolinaldimine](olefin)rhodium perchlorate, [Rh[2-C_5H_4NCH=N-(S)-CHMePh]$_2$(L)]ClO_4(L = fumaronitrile(FN), maleic anhydride(MA), dimethyl fumarate(DF)).

Fumaronitrile(0.05 g, 0.64 mmol) and **I**(0.4 g, 0.64 mmol) was dissolved in dichloromethane(10 ml), and stirred for 20 min, during which time the color of the solution changed from violet to orange. The solution was evaporated to dryness under reduced pressure to give the crude FN adduct, which was recrystallized from dichloromethane-petroleum ether to yield o.32 g (71 %) of product. The crystals were solvated with a quarter mole of dichloromethane, $[\alpha]_D^{24}$ -110°(c 0.100, CH_3CN); Λ_M = 155 $ohm^{-1}cm^2mol^{-1}$; $\nu(C\equiv N)$ 2204 cm^{-1}. *Anal*. Calcd for $C_{32}H_{30}N_6O_4ClRh \cdot 1/4CH_2Cl_2$: C, 53.63; H, 4.26; N, 11.64 %. Found: C, 53.75; H, 4.25; N, 11.86 %.

An equimolar solution of I and MA or DF in dichloromethane was stirred for 10 min, filtered and evaporated to dryness under reduced pressure to give analytically pure MA(83 %) or DF adduct (90 %) without recrystallization. The MA adduct: Λ_M = 133 ohm^{-1}-cm^{2}mol^{-1}; ν(C=O) 1792 and 1720 cm^{-1}. Anal. Calcd for $C_{32}H_{30}$-N_4O_7ClRh: C, 53.31; H, 4.19; N, 7.77 %. Found: C, 53.34; H, 4.22; N, 7.87 %. The DF adduct: Λ_M = 150 ohm^{-1}cm^{2}mol^{-1}; ν(C=O) 1691 cm^{-1}. Anal. Calcd for $C_{34}H_{36}N_4O_8ClRh$: C, 53.24; H, 4.73; N, 7.30 %. Found: C, 53.06; H, 4.58; N, 7.32 %.

Bis[N-(S)-α-phenylethylpicolinaldimine](dimethyl acetylenedicarboxylate)rhodium perchlorate, $[Rh[2\text{-}C_5H_4NCH{=}N\text{-}(S)\text{-}CHMePh]_2\text{-}(DAD)]ClO_4$.

An equimolar solution of I and DAD in dichloromethane was stirred for 1 hr, followed by evaporation to dryness under reduced pressure. The resulting product was recrystallized from hot methanol to afford orange needles(65 %); $[\alpha]_D^{23}$ +43.0°(c 0.100, CH_3CN); Λ_M = 190 ohm^{-1}cm^{2}mol^{-1}; ν(C≡C) 1802 cm^{-1}; ν(C=O) 1656 cm^{-1}. Anal. Calcd for $C_{34}H_{34}N_4O_8ClRh$: C, 53.38; H, 4.48; N, 7.32 %. Found: C, 53.19; H, 4.45; N, 7.38 %.

Bis(N-benzylpicolinaldimine)(dimethyl fumarate)rhodium perchlorate, $[Rh(2\text{-}C_5H_4NCH{=}NCH_2Ph)_2(DF)]ClO_4$.

The complex was prepared by the reaction of II with DF as described in the DAD adduct of I. Recrystallization from hot ethanol gave hygroscopic crystals(50 %) which contained two molecules of water as confirmed by IR and ^{1}H NMR: Λ_M = 160 ohm^{-1}-cm^{2}mol^{-1}; ν(O-H) 3550 cm^{-1}; ν(C=O) 1683 cm^{-1}. Anal. Calcd for $C_{32}H_{32}N_4O_8ClRh\cdot 2H_2O$: C, 49.59; H, 4.63; N, 7.23 %. Found: C, 49.81; H, 4.46; N, 7.30 %.

Separation of Diastereomers

A hot methanol solution of the MA or DF adduct of I was allowed to stand at room temperature for a few hours to give orange needles(the MA adduct); $[\alpha]_D^{24}$ +97.9°(c 0.114, CH_3CN), or a red needles(the DF adduct); $[\alpha]_D^{24}$ -419°(c 0.100, CH_3CN). The optical rotations of these compounds were constant even after repeated crystallization, indicating the presence of one of the diastereomers. Some attempts to separate the other of the diastereomeric pair from the mother liquor were unsuccessful.

Physical Measurements

The electric conductivity, infrared, and ^1H NMR spectra were measured as described in Chapter I. Optical rotations were measured on a Perkin-Elmer 241 polarimeter using an 1 dm cell.

III-3. RESULTS AND DISCUSSION

Bis(chelate) Complexes

I, II, and III are stable under dry nitrogen, but they are gradually decomposed in air.

Variable temperature ^1H NMR spectra of I in C_6H_5CN are depicted in Fig. 1, which shows two doublets of the CH_3 signals at 24°C. With raising the temperature, these signals become broad and coalesce at about 80°C. The spectra were reproducible in the 24°∼80°C range, while the complex was decomposed on heating up to 90°C. Further, the appearance of spectra at

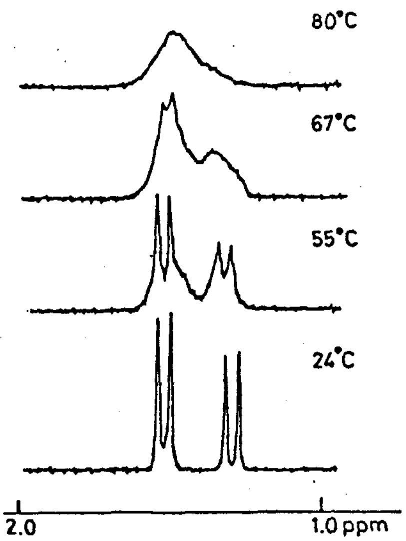


Fig. 1. Variable temperature ^1H NMR spectra of the CH_3 protons of $\{Rh[2\text{-}C_5H_4NCH{=}N\text{-}(S)\text{-}CHMePh]_2\}$-$ClO_4$ in C_6H_5CN.

each temperature was little altered, not only by changing the concentration but on addition of $2\text{-}C_5H_4NCH{=}N\text{-}(\underline{S})\text{-}CHMePh$ to the parent solution. There may be three possible explanations for the temperature dependence of the spectra; (i) *cis*-*trans* isomerization around the rhodium center, (ii) the conformational restriction of rotation about the asymmetric carbon-imine nitrogen bond, and (iii) an inversion of the distorted planar configuration at the rhodium center. *II* and *III* in C_6H_5CN, however, exhibit only one set of benzyl and *tert*-Bu proton signals, respectively, which show no change in the same temperature range. This indicates that the *cis*-*trans* isomerization is unlikely. The second possibility is also unlikely, because the restricted rotation of this sort has not been observed not only in Mo(II) and W(II) complexes of the chiral ligand used here[3] but also in the olefin or acetylene adducts of *I*. On the other hand, an X-ray structure analysis has demonstrated that $[Pd(bipy)_2]^{2+}$(bipy = α,α'-bipyridine) adopts a distorted planar configuration, in which two ligand planes are twisted to each other.[8] A similar distorted structure may be assumed for I which is sterically crowded. It may, therefore, be suggested that I involves two diastereomers due to the right-handed and left-handed helicities, which predict the appearance of two sets of proton signals. The inversion of helicity in I may cause diastereomeric averaging at elevated temperatures. An analogous inversion has been reported for a series of bis(β-aminothionato)zinc(II) complexes.[9] Thus, the inversion at the rhodium center is most likely to occur.

Although the ^{1}H NMR spectra indicate that I, II, and III all exist as a single geometrical isomer, the stereochemistry could not be determined by their infrared and ^{1}H NMR spectra. Molecular models, however, show that steric repulsions are minimized when the imine nitrogen atoms of two ligands are located in *trans* positions to each other.

Adducts of the Bis(chelate) Complexes

The DF adduct of II exhibits an AB type quartet of the CH_2 proton signals at δ4.95 and 4.73 ppm(^2J = 13 Hz), which indicates that the metal center becomes chiral upon coordination of DF. On the other hand, the DF adduct of I displays two sets of the olefinic and C-CH_3 proton signals with different intensities designated as α and β in Fig. 2, although two DF-CH_3 signals are superimposed. This is suggestive of the existence of two diastereomers, at least in the DF adduct of I. Similar two sets of proton signals are observed in the FN, MA, and DAD adducts of I(Table I). In addition, the MA

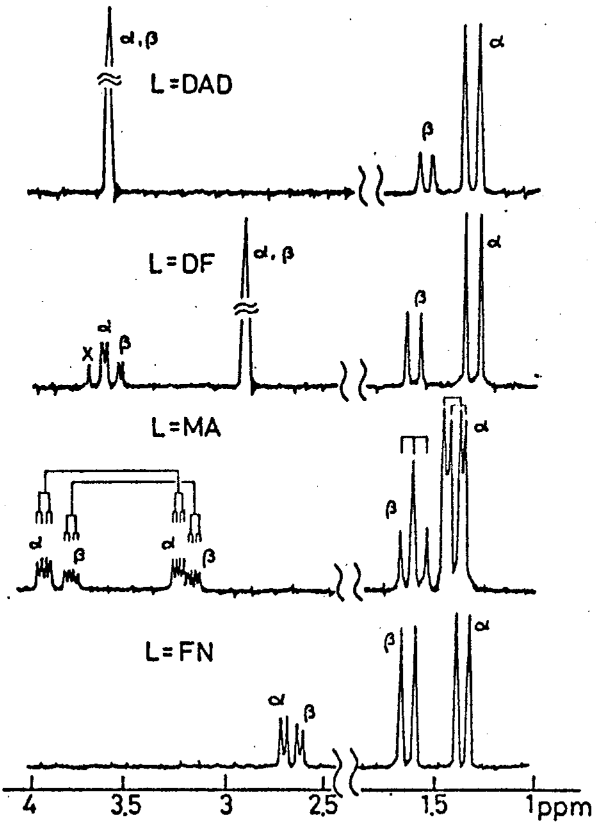


Fig. 2. ^1H NMR spectra of $\{Rh[2\text{-}C_5H_4NCH{=}N\text{-}(S)\text{-}CHMePh]_2(L)\}ClO_4$ at equilibrium in CD_3CN at 25°C. The signal indicated by x (L = DF) is due to the CH_3 protons of dissociated DF.

TABLE 1

^1H CHEMICAL SHIFTS (δ, ppm) OF $\{Rh[2\text{-}C_5H_4NCH{=}N\text{-}(S)\text{-}CHMePh]_2\}ClO_4$ AND THEIR ADDUCTS WITH OLEFINS OR ACETYLENE AT 25°C

Olefin or acetylene [a]	Solvent	Picolinaldimine [b]		Olefin or acetylene		Isomer ratio [f]
		CH_3 [c]	H(6) [d]	CH [e]	CH_3	
—	C_6H_5CN	1.23, 1.56	8.72, 8.62			
	CD_3CN	1.29, 1.50	8.76, 8.60			
FN	CD_3CN	α 1.35	8.76	2.69		54
		β 1.63	8.76	2.61		46
MA	CD_3CN	α 1.41, 1.37	8.62	3.93, 3.25		64
		β 1.64, 1.56	8.76	3.78, 3.16		36
DF	CD_3CN	α 1.34	8.58	3.63	2.91	55
		β 1.60	8.51	3.55	2.91	45
	$CDCl_3$	α 1.26	8.83	3.59	3.00	60
		β 1.67	8.67	3.53	3.02	40
DAD	CD_3CN	α 1.34	8.72		3.63	74
		β 1.56	8.59		3.63	26

[a] The abbreviations used are as follows: FN = fumaronitrile, MA = maleic anhydride, DF = dimethyl fumarate and DAD = dimethyl acetylenedicarboxylate. [b] α and β correspond to those in Fig. 2. [c] $^3J(CH_3{-}CH)$ 6.5 Hz. [d] $^3J(HH)$ 1.5 Hz. [e] $J(^{103}Rh{-}H)$ 2 Hz. [f] Determined from the intensity of the CH_3 signals of $2\text{-}C_5H_4NCH{=}N\text{-}(S)\text{-}CHMePh$.

adduct shows two AB type quartet signals due to the olefinic protons of diastereomers, and each signal is further split into a doublet owing to coupling with the ^{103}Rh nucleus(Fig. 2). The intensity ratio of two sets of signals(α/β) in these four adducts more or less varies with temperature and solvent.

Stereochemistry

When two unsymmetrical chelates, 2-C_5H_4NCH=N-R, and one molecule of olefin or acetylene occupy six coordination sites of an octahedron as in the DF adduct of II, three geometrical isomers, A, B, and C, are possible, as shown in Fig. 3.

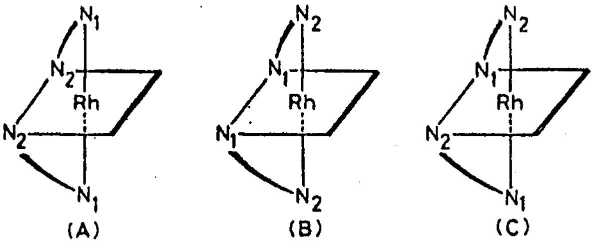


Fig. 3. Possible geometrical isomers of [Rh(2-C_5H_4NCH=N—R$)_2$(L)]·ClO_4: L = olefin or acetylene; N_1 = imine nitrogen, N_2 = pyridine nitrogen.

In the A and B isomers only one NMR signal is expected to occur for each of the different protons in the 2-C_5H_4NCH=N-R ligand, while C predicts the appearance of two sets of signals with identical intensity. The spectrum of the DF adduct of II showed only one set of resonances. This was also the case with each of the diastereomeric pairs of the FN, DF, and DAD adducts of I. The geometrical isomer would therefore be A or B. The C-CH_3 signals of the MA adduct of I appeared as two kinds of doublets(Fig. 2), because of the diamagnetic anisotropy of the carbonyl groups of MA.[10] This anisotropy, however, hardly affects the chemical shift of the H_6 proton of the pyridine ring(Table I). Thus, the MA adduct of I is more likely to assume the A isomer. Almost unchanged chemical shifts of the H_6 proton in all the adducts predict that the FN, DF, and DAD adducts of I and the DF adduct of II adopt the same configuration as the MA adduct of I.

The A isomer of the FN and DF adducts of II may theoretically involve four possible optical isomers; two diastereomeric pairs of enantiomers owing to chiralities of the rhodium center (Δ or Λ)[11] and of the coordinated olefin carbons(R or S)[4], as seen in Fig. 4. When the chiral ligand, $2\text{-}C_5H_4NCH{=}N\text{-}(S)\text{-}CHMePh$, is used, each optical isomer bears a diastereomeric relation to the others.

The ^1H NMR pattern of the DF adduct of II was little changed in the 60°～-50°C range. Similar rhodium complexes, $[Rh(p\text{-}CH_3C_6H_4NC)_4(TCNE)]ClO_4$(TCNE = tetracyanoethylene) and $Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)(FN)I$, exhibit the temperature dependences to give their limiting spectra at -35° and -50°C, respectively.[12]

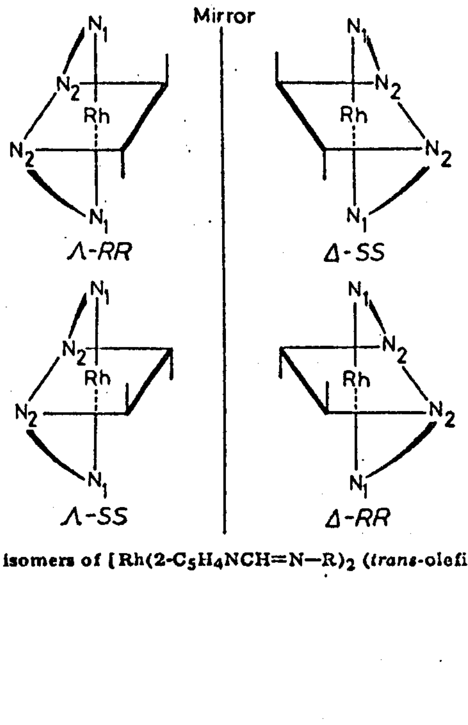


Fig. 4. Possible optical isomers of $[Rh(2\text{-}C_5H_4NCH{=}N{-}R)_2$ (*trans*-olefin)$]ClO_4$ for the geometrical isomer of A.

Thus, the fast dynamic process for the present adducts may be excluded on the NMR time scale. The occurrence of one set of the ^{1}H signals in the DF adduct of II implies either the formation of only one pair of enantiomers or the coincidence of two resonances of the diastereomeric pair. Similarly, two sets of resonances observed in the DF and FN adducts of I suggest either the existence of only two diastereomers or the coincidence of spectra. Attempts to resolve this question by the use of shift reagents were unsuccessful. Thus, it has not been able to be elucidated whether the enantiotopic face of prochiral olefins(DF, FN) is differentiated or not.

Stereoselectivity

^{1}H NMR measurements indicated that two diastereomers equilibrated in an CD_3CN solution are formed in the ratios of 64:36 and 74:26 for the MA and DAD adducts of I, respectively. Thus, the stereoselectivity in the two diastereomers, arising from the chirality of the rhodium center, are 28 and 48 % respectively. We have carried out an approximate conformational analysis[13] of the asymmetric (S)-carbon moiety on the imine nitrogen by considering the bulkiness of phenyl groups. The result indicates that the conformations of D and E being diastereomeric to each other, shown in Fig. 5, are preferable

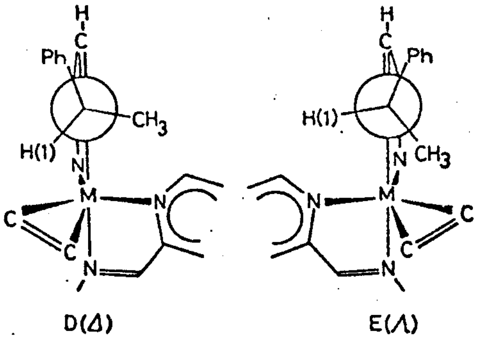


Fig. 5. Preferred conformations of two diastereomers of the MA or DAD adduct of I; the view along one of the asymmetric carbon-imine nitrogen bonds.

to the other rotational isomers. The stereoselectivity on equilibration may be mainly related to the difference in the steric repulsion between the H(1)-proton or CH_3 group and olefin or acetylene. The repulsion of the H(1)-proton with olefin or acetylene in D would be small. It is therefore suggested that the configuration of the major diastereomer(the α signal in Fig. 2) of the MA and DAD adducts is Δ, and that of the minor diastereomer(the β signal in Fig. 2) Λ. This assignment is consistent with the observation that the splitting of the β signal of the MA adduct is larger than that of the α signal. The large splitting of the former may be expected from the fact that in E the CH_3 protons are located closely to MA, which exerts an anisotropy effect.[10]

Epimerization Mechanism

The separated MA or DF adduct of I is subject to configurational interconversion in solution, as confirmed by the ^1H NMR and optical rotation measurements; the solution immediately after dissolution in CD_3CN exhibits only one set of the α signals in Fig. 2, but the β signals gradually appear in the spectra. A corresponding change in the optical rotation at 589 nm was observed(Fig. 6). The rate of epimerization was

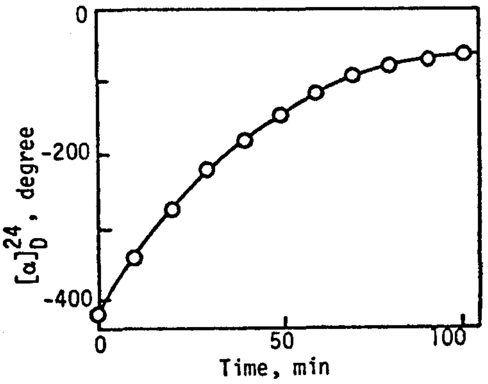


Fig. 6. The change of optical rotations at 589 nm of the separated $[Rh(2\text{-}C_5H_4NCH{=}N\text{-}(\underline{S})\text{-}CHMePh)_2(DF)]ClO_4$ with time in CH_3CN at 24°C.

obtained in an CH_3CN solution at 24°C($1 \times 10^{-3} \sim 10^{-4}$M). The epimerization of both adducts was found to obey first order kinetics. The rate of epimerization of the DF adduct($3.34 \pm 0.20 \times 10^{-2}$ min^{-1}) is faster than that of the MA adduct($6.90 \pm 0.31 \times 10^{-3}$ min^{-1}). There may be two possible mechanisms, intra- and intermolecular, for the epimerization. When MA or DF was added to the solution of the corresponding adduct, a decreasing rate of epimerization was observed. At the same time, a very weak CH_3 signal of the dissociated DF appear at δ3.75 ppm in the course of epimerization. These observations do not contradict the intermolecular mechanism of epimerization, which involves the dissociation of olefin. It may be conceivable that the slower epimerization rate in the MA adduct reflects a stronger rhodium-olefin bond than in the DF adduct. Thus, the present interconversion appears to occur <u>via</u> the S_N1 mechanism. This is in contrast to the olefin complexes of platinum(II), such as PtCl(<u>L</u>-prolinato)(<u>trans</u>-2-butene), whose interconversion was reported to take place through an S_N2 mechanism.[14]

III-4. SUMMARY

Some bis(N-substituted picolinaldimine)rhodium perchlorates, $[Rh(2\text{-}C_5H_4NCH{=}N\text{-}R)_2]ClO_4$(R = (<u>S</u>)-CHMePh(<u>I</u>), CH_2Ph(<u>II</u>), <u>tert</u>-Bu(<u>III</u>)) and their adducts with fumaronitrile(FN), maleic anhydride(MA), dimethyl fumarate(DF), and dimethyl acetylenedicarboxylate(DAD) were prepared. The stereochemistry of the adducts is discussed in terms of the geometrical isomers and optical isomers due to the chiralities both of the metal center and of the coordinated olefin. A stereoselectivity was found in the formation of the MA and DAD adducts of I, which yielded two diastereomeric complexes. Furthermore, one of diastereomers of the MA and DF adducts was isolated by fractional crystallization. The epimerization of these was observed and the mechanisms are discussed.

III-5. REFERENCES

1. (a) H. B. Kagan and T-P. Dang, J. Am. Chem. Soc., 94, 6429 (1972); (b) W. S. Knowles, M. J. Sabacky, B. D. Vineyard, and D. J. Weinkauff, ibid., 97, 2567 (1975); (c) S. Siegel and D. W. Ohrt, Tetrahedron Lett., 5155 (1972).
2. Y. Izumi, Angew. Chem. Int. Ed., 10, 871 (1971).
3. H. Brunner and W. A. Herrmann, Chem. Ber., 105, 772, 3600 (1972).
4. G. Paiaro, Organometal. Chem. Rev.,(A), 6, 319 (1970).
5. A. Ault, Org. Synth., Coll. Vol. 5, 932 (1973).
6. W. Theilaker and H. G. Winkler, Chem. Ber., 87, 691 (1954).
7. R. Cramer, Inorg. Synth., 15, 14 (1974).
8. M. Hinamoto, S. Ooi, and H. Kuroya, J. Chem. Soc., Chem. Commun., 356 (1972).
9. S. S. Eaton and R. H. Holm, Inorg. Chem., 10, 1446 (1971).
10. J. A. Pople, W. G. Schneider, and H. J. Bernstein, High-resolution Nuclear Magnetic Resonance, McGraw-Hill,

New York, N. Y., 1959, p176.

11. K. A. Jensen, Inorg. Chem., 9, 1 (1970).
12. T. Kaneshima, K. Kawakami, and T. Tanaka, Inorg. Chem., 13, 2198 (1974).
13. E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, Conformational Analysis , Wiley, New York, 1965, p13.
14. K. Konya, J. Fujita, H. Kido, and K. Saito, Bull. Chem. Soc. Jpn., 45, 2161 (1972).

CONCLUSION

This study was undertaken to elucidate the metal-olefin or -acetylene binding processes. The results of the present work are summarized as follows.

(1) Several isocyanide iridium(I) complexes $[Ir(RNC)_4]X$(I) (R = p-$CH_3C_6H_4$, X = I; R = p-$CH_3OC_6H_4$, X = I and PF_6) and $[Ir(RNC)_2(PPh_3)_3]ClO_4$(II) (R = p-$CH_3C_6H_4$ and p-$CH_3OC_6H_4$) were prepared. I is suggested to adopt an oligomeric structure involving Ir to Ir interaction. The reactions of II with olefins or acetylene give the complexes $[Ir(RNC)_2(PPh_3)_2$(olefin or acetylene)$]ClO_4$ (R = p-$CH_3C_6H_4$; olefin or acetylene = tetracyanoethylene(TCNE), fumaronitrile(FN), maleic anhydride(MA), or dimethyl acetylenedicarboxylate(DAD)). The reactivity of II to olefins and acetylene is comparable to that of the Vaska's complex, $IrCl(CO)(PPh_3)_2$.

(2) Kinetics of the addition reactions of TCNE to some rhodium(I) and iridium(I) complexes, trans-$[Rh(RNC)_2L_2]ClO_4$(R = p-$CH_3OC_6H_4$, p-ClC_6H_4, and C_6H_{11} and L = PPh_3 and $P(OPh)_3$), trans-$RhX(CO)L_2$(X = Cl, L = P(p-$CH_3OC_6H_4)_3$, P(p-$CH_3C_6H_4)_3$, PPh_3, P(p-$ClC_6H_4)_3$, PPh_2Me, $AsPh_3$, P(O-o-$CH_3C_6H_4)_3$, $P(OPh)_3$; X = Br, I, NCO, NCS, L = PPh_3), and trans-$IrCl(CO)(PPh_3)_2$, in acetonitrile, acetone, tetrahydrofuran(THF), and benzonitrile were investigated employing the stopped-flow technique. The reaction is accelerated by electron-releasing substituents of phosphines and isocyanides. Furthermore, the reaction rate increases with increasing solvent polarity

in the order of THF $<$ acetone $<$ acetonitrile or benzonitrile. The activation parameters are also strongly dependent on solvents. From these results, it was concluded that the reaction involves a dipolar activated complex formed by the nucleophilic attack of the metal complex on TCNE.

(3) Some bis(N-substituted picolinaldimine)rhodium perchlorates, $[Rh(2\text{-}C_5H_4NCH{=}N\text{-}R)_2]ClO_4$, (III, R = (S)-CHMePh; IV, CH_2Ph) and their adducts with FN, MA, DAD, and dimethyl fumarate (DF) were prepared. A stereoselectivity was found in the formation of the MA and DAD adducts of III; one of diastereomers of the MA and DF adducts was isolated by fractional crystallization. The epimerization of these adducts was found to occur via the intermolecular mechanism, which involves the dissociation of olefin.