Acrylonitrile adducts and related systems

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ACRYLONITRILE ADDUCTS AND
RELATED SYSTEMS

A Thesis Submitted to
The University of Durham

by

Paul Gideon Huggett, B.Sc.
(Grey College)

For the Degree of
Doctor of Philosophy
December 1979

To My Family

"Why is this thus? What is the Reason for this thusness"

Artemus Ward 1834-1867

"Believe it, or not"

R.L. Ripley 1893-1949

ACKNOWLEDGEMENT

I should like to thank Dr. K. Wade, under whose supervision this work was carried out, for his encouragement and advice. I should also like to thank Drs. J.A. Daniels and J.R. Jennings of I.C.I. Ltd. for valuable discussions.

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I would also like to thank Mrs. Marion Wilson for her unerring expertise in the typing and correcting of this thesis.

Lastly my thanks are due to my friends in Durham without whose moral as well as technical support this work would not have been as enjoyable as it was.

MEMORANDUM

The work described in this thesis was carried out by me in the Chemistry Department of the University of Durham between October 1976 and September 1979 except for parts of Chapters Three and Five which were carried out with the collaboration of Mr. K. Manning of this Laboratory. I declare that this work has not been submitted for any other degree. This thesis is my original work, except where indicated by reference to other work.

P.G. Huggett,
December 1979

Parts of this work have been published in or submitted for publication to the following Journals:

"The relative Lewis acidities of $SiCl_4$, $GeCl_4$, $SnCl_4$ towards acrylonitrile: vapour pressure - composition studies"

J.A. Daniels, J.R. Jennings, P.G. Huggett, K. Wade, Inorg.Nucl.Chem.Lett., 14, 445 (1978)

"The relative Lewis acidities of silicon tetrachloride, germanium tetrachloride and tin tetrachloride towards acetonitrile, acrylonitrile, ethyl acetate, diethyl ether and tetrahydrofuran: vapour pressure - composition studies"

Paul G. Huggett, Kenneth Manning, Kenneth Wade, J.Inorg.Nucl.Chem., In Press.

"^{35}Cl nuclear quadrupole resonance studies on some tin IV chloride adducts"

Paul G. Huggett, Roderick J. Lynch, Thomas C. Waddington, Kenneth Wade

J.C.S., Dalton (in press).

THESIS ABSTRACT

The coordination chemistry of acrylonitrile (ACN) has been studied with the long term view of modifying the reactivity of ACN to a Lewis acid.

The first chapter of this work is a review of ACN coordination and organometallic chemistry up to July 1979 together with a comprehensive tabular summary of the literature.

The coordination of ACN with relatively hard Lewis acids such as $SnCl_4$, $TiCl_4$, $ZnCl_2$, etc., has been shown to occur via the C≡N lone pair and the repulsive interactions between ACN (as well as acetonitrile, diethyl ether, ethyl acetate and tetrahydrofuran) and $GeCl_4$ and $SiCl_4$ have been demonstrated by vapour pressure/composition studies.

The stereochemistry of the solid adducts $SnCl_4L_2$ where L = MeCN, Ch_2CHCN, Bu^t, $NC(CH_2)_nCN$ (n = 1-4), 1,4 $C_6H_4(CN)_2$, THF, Me_2SO and tetrahydrothiophene was investigated by nuclear quadrupole resonance and infra-red spectroscopy.

The hydrostannation of nitriles by HCl and $SnCl_2$ has been shown to yield β cyanoethyl tin trichloride with ACN but dimeric salts with an amidinium structure with alkyl and aryl nitriles.

Finally the stoichiometric dimerization of ACN to solely adiponitrile by cobalt chloride and an electropositive metal (M = Mg, Mn, Zn) in a variety of solvents has been investigated and several plausible mechanisms proposed.

CONTENTS

CHAPTER ONE

An introduction to the Coordination Chemistry of Acrylonitrile

1.1 Introduction

Moureu discovered acrylonitrile (ACN) in 1893 and showed it to be the nitrile of acrylic acid.[1] Between then and the start of World War II ACN remained a laboratory curiosity until military demands brought about the development of the first oil and petrol resistant nitrile rubbers. At the conclusion of hostilities the demand for nitrile rubbers slackened and new uses for ACN monomer had to be found. The first and most important of these was the development of acrylic fibres and surface coatings. Subsequently ACN has found uses as a chemical intermediate in the preparation of adipic acid used for nylon 6.6 production and as a versatile cyanoethylating agent.

The object of this chapter is to review only the coordination and related chemistry of ACN. The organic chemistry of ACN has been reviewed in reference 2 and organonitrile chemistry in general in reference 3.

A number of organometallic chemistry reviews have included information relevant to ACN. Walton[4] and more recently Storhoff and Lewis[5] have reviewed organonitrile complexation in addition to references 6-8 whilst general transition metal olefin complexes are reviewed in references 9 and 10 with thermodynamic data in reference 11. More specific reviews making reference to ACN include platinum and palladium complexes,[12] bis(ACN)nickel $\underline{\overline{0}}$,[13] and adducts with Group IVA acceptors.[14] The reaction of ACN with organometallic moieties has been discussed in references 15-18.

This review sets out to survey the coordination chemistry of acrylonitrile up to mid 1979 with particular reference to the ability of ACN to act as a π and/or σ donor with the implications towards bonding, stability and reactivity. A comprehensive table is presented in this chapter which divides the literature on the basis of Lewis acid studied, its position in the periodic table and the type of study that has been conducted. The column headed 'stoichiometry' indicates the number of ACN molecules incorporated in the adduct. Where no stoichiometry is given the reference has studied the reaction of ACN with the Lewis acid.

In the text the literature is discussed on the basis of the type of study. Since there have been relatively few ACN adduct crystal structures determined they are discussed at some length since they provide useful illustration of the modes of coordination of acrylonitrile. We will then discuss the remaining adducts, the structures of which have been proposed on the basis of usually vibrational and magnetic spectroscopy, distinguishing those containing solely N bonded ACN from those containing ACN π bonded through the C=C double bond. Finally the reactions of ACN with a range of Lewis acids will be discussed.

TABLE 1.1 Adducts of Acrylonitrile

Lewis Acid	Stoichiometry	Spectroscopic	Reactivity	Other
GROUP IA				
$LiNO_3$	1			131
LiCl	1			131
LiMe	-			132
GROUP IIA				
$MgNO_3$	1			131
MgX_2+R_3N, X=Cl,Br,I				106
$Mg(SbCl_6)_2$	6	291	291	
$Mg(InCl_4)_2$	3	291	291	
GROUP IIIA				
BCl_3	1	60,133	134	
$BEtCl_2$	1	53		
$AlMe_3$	1	73,74,75, 292	73,74,75, 292	
$AlEt_3$	1	53,135	53	
$AlBu^i{}_3$	1	143	143	
$AlMe_2Cl$	1	74,75	74,75	
$AlEt_2Cl$	1	53	53	
AlEt(OEt)Cl	1	53	53	
$AlHBu^i{}_2$	-		73	
$AlMeCl_2$	1	53,74,75	53,74,75	
$AlEtCl_2$	1	53,135, 136,137 138,139	53	
$Al(OEt)Cl_2$	1	53	53	
$Al_2Et_3Cl_3$				127

TABLE 1.1 (contd.)

Lewis Acid	Stoichiometry	Spectroscopic	Reactivity	Other
$AlCl_3$	1	53	53	
	2			
	-	50,53,138		
$AlCl_3+R_3N$				103,107
GROUP IVA				
SnR_3H	-		76,78,79	
SnR_2H_2	-		77,79,290	
$SnCl_4$	2	46,47,149		
	1	53		
	-	138		
Sn+HCl	-			144
GROUP VA				
$PCl_3:NPCl_3^+$	-			145
PR_3	-			8,145,184
$SbCl_5$	1	45,68	45	
$BiPh_3$	-			98
GROUP IVB				
$TiCl_4$	2	43,47,49 146	49,146,147	
	1	53,142,146	142	
$TiCl_4+R_3N$	-		103,107	
$TiCl_3$	3	49	49,146	
$TiCl_3+R_3N$	-		107	
$TiCl_3+Mg+ROH$	-		117	
$TiBr_3$	3	43		

TABLE 1.1 (contd.)

Lewis Acid	Stoichio-metry	Spectro-scopic	Reactivity	Other
$ZrCl_4$	2	43		
GROUP VB				
$VOCl_3$	-			138
$VOCl_2$	2	49	49	
	-		148	
VCl_4	2	142	142	147
	4	142	142	
VCl_3	2		149	
	3	49	49	
	-		148	
VCl_3+Mg+ROH	-		117	
VCl_2+R_3N	-		103,107	
V (acac)$_3$	-		150	
VBr_3	3	43	43	
VCl_2	-	148	151	
$TaCl_5$	1	43,44		
	-	152,153		
$TaCl_4$		43	43	
$TaMeCl_4$	1	154	154	
$NbCl_5$	1	43,44		
	-	152		
$NbMe_2Cl_3$	1	154	154	
$NbCl_4$	2	43		
GROUP VIB				
$CrCl_3$	3	47,49	155,156	
	-	148		

TABLE 1.1 (contd.)

Lewis Acid	Stoichio- metry	Spectro- scopic	Reactivity	Other
$Cr(ClO_4)_3$	3		156	
$(CrCl_2L_4)Cl$	4		156	
$CrCl_2$	-	148		
CrX_2+R_3N X=Cl,Br,I	-		106	
$Cr(CO)_5$	1	54,157,158	157	
$Cr(CO)_4$	2	33	33	
$Cr(CO)_2L$, L=arene	1	54		
$MoCl_3$	3	48	48	
	-	148		
$(R_4N)_2(MoCl_5)^{2-}$	1	48	48	
$Mo(CO)_6+Ph_3P$	-			159
$Mo(CO)_4$	2	33	33	
$Mo(CO)_3$	3	33	33,160	
$Mo(CO_3(Ph_3P)$	1		161	
$Mo(CO)_2$	2	41,162	41	
$Mo(CO)_2(Ph_3P)_3$	1	163	163	
$Mo(CO)_2(Ph_3P)_2$	2	163,164	163,164	
$Mo_2(CO)_4(PBu_3)_4$	2	25		
$MoCp_2$	1	85,165	85,165	
$MoCp_2H_2$	-		165	
WCl_6	-		166	
$WCl_4.NCCl_2R$	2		167	
WCl_4	1		167	
$W(CO)_6+Ph_3P$	-			159
$W(CO)_5$	1	33,54,157 168	33,154,168	

TABLE 1.1 (contd.)

Lewis Acid	Stoichio- metry	Spectro- scopic	Reactivity	Other
$W(CO)_4$	2	33	33	
$W(CO)_3$	3	33,168	33,168	
WCp_2	1	165	165	
GROUP VIIB				
$MnCl_2$	2			131
	1	47,49	49	
MnX_2+R_3N,	-		106	
X=Cl,Br,I				
$Mn(SbCl_6)_2$	6	291	291	
$Mn(InCl_4)_2$	3	291	291	
$Mn_2(CO)_9$	1	169	169	
$MnCp(CO)_2$	1	170	170	
$Re(N{=}NCOPh)Cl_2(PPh_3)_2$	1	280		
GROUP VIII				
$FeCl_3$	-	148	49,171	172
$FeCl_3+Mg+ROH$	-		117	
$Fe(acac)_3+RNC$	-		109	
$FeCl_2.2FeCl_3$	6	47,49		
$FeCl_2$	1	47,49		
$FeCl_2+Mn$	-		114	
$Fe(SbCl_6)_2$	6	291	291	
$Fe(InCl_4)_2$	3	291	291	
$FeCl_3+R_3N$	-		102,103,107	
$Fe(acac)_2+RNC$	-		109	
$Fe(CNC_6H_4Me)_5^{2+}$	1	173	173	174

TABLE 1.1 (contd.)

Lewis Acid	Stoichiometry	Spectroscopic	Reactivity	Other
$Fe^{2+}(Anion)^{2-}$, Anion=$Fe(CO)_4{}^{2-}$, $Fe_2(CO)_8{}^{2-}$, $Fe_3(CO)_{11}{}^{2-}$, $Fe_4(CO)_{13}{}^{2-}$	1	173	173	
FeR_2bipy			175	
$FeCp(CO)_2{}^{2+}(Anion)^{2-}$, Anion=$BF_4{}^-$, $PF_6{}^-$	1	177	177	176
$FeCp(CO)_2H$	-		83	
$Fe(CO)_4$	1	19,20,31, 178,179, 180	19,31,181	178,179, 182,183, 184
$\{Fe(CO)_3\}_2$	2	26		
$Fe(CO)_5+H^+$	-		112	
$Fe(CO)_4H^-$	-		112	
$Fe_2(CO)_8H^-$	-		112	
$Fe_3(CO)_{11}H^-$	-		112	
$Fe(PF_3)_4$	1	185		
$FeC_7H_9(CO)_2PF_6$	1	186		
$RuCl_3$	-	101		102
$Ru(NH_3)_5Cl_3$	1	64	64	
$Ru(MPh_3)X_3$, X=Cl,Br;M=P,As	1	187,188, 189	187,188, 189	
$RuCl_3+BiPh_3$	-		98	
$RuCl_3.(H_2O)_3+H_2$	-		62,91,92, 130,190,191	
$RuCl_3(Ph_3P)_3+H_2$	-		193,191	
$Ru(OAc)_2OH+H_2$	-		192,193	
$Ru(acac)_3+H_2$	-		62,93	

TABLE 1.1 (contd.)

Lewis Acid	Stoichiometry	Spectroscopic	Reactivity	Other
$Ru(OH)_3+H_2$	-		192	
$\{Ru_3(OAc)_6(H_2O)_3\}OAc$	-		130	
$\{Ru_3(EtCO_2)_6(H_2O)_3\}O_2CEt$	-		130	
$RuCl_2$	4	194	94,95,194	
	3	92	92	
	2	93	93	
RuI_2	4	194	194	
$Ru(NH_3)_5Cl_2$	1	64	64	
	-	65		
$Ru(Ph_3P)_2Cl_2$	2	195	62,94,195	
$Ru(Ph_3As)_2Cl_2$	2	187	187	
$Ru(H_2O)Cl_2$	2		94	
$RuCl_2(CO)COD$	1	196	196	
$Ru(acac)_2CO$	1		96	
$RuX_2(CO)_3$, X=Cl,Br		197	197	
$Ru(H_2NCH_2CH{:}CH_2)$ $bipy_2{}^{2+}(PF_6{}^-)_2$	1		198	
$Rubipy_2{}^{2+}(PF_6{}^-)_2$			198	
$\{RuCl(\sigma C_3H_5)(CO)_2\}_2$	2	199	199	
$RuCl(\sigma C_3H_5)(CO)_2Ph_3P$	1	199	199	
$Ph_3BzP^+(RuCl_3CO)^-$	2	200	200	
$RuCl_2(CO)_2py$	-		62	
$Ru_2(O_2CR)_4Cl+H_2$	-		201	
$Ru_2(O_2CR)Cl$	-		99	
$RuCl(Ph_3P)_2{}_2$			94	
$Ru(SbPh_3)_3$			191	

TABLE 1.1 (contd.)

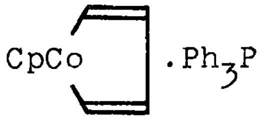
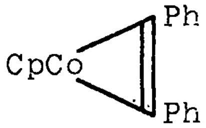
Lewis Acid	Stoichiometry	Spectroscopic	Reactivity	Other
$OsHClCO\{P(C_6H_{11})_3\}_2$	1	202		
$CoClDMG_2$	1	203		
$CoBrDMG_2$	1	203		
$CoClDMG_2.py$	-		204,205	
NaCo(N-SGT)	-		206	
$Co(CN)_5H^{3-}$	-		80,207,208	
$Co(NH_3)_5(ClO_4)_3$	1	209	209,293	
$CoCl_2$	1	47,49	49	281
CoX_2+R_3N X=Cl,Br,I	-		102,103,107,108	
CoX_2+M, X=Cl,Br,I;M=Mg,Zn,Mn	-		113,115,116,119,210	
$Co(NO_3)_2$	-			131
$Co(SbCl_6)_2$	6	291	291	
$Co(InCl_4)_2$	3	291	291	
$Co(acac)_3+C_6H_{11}NC$	-		109	
	-		211	
	-		212	
$K^+ \; Co(CN)_2(PEt_3)_2{}^-$	1			214
$CoH.N_2(Ph_3P)_2$	1		213	215
$CoMe(Ph_3P)_2$	1		216	
$CoDMG_2{}^-$	-		111	
$Co(CO)_2$	1		217	
$Co_2(CO)_8$	-		112,218	
$Co_2(CO)_8.PhC{\equiv}CH$	-		219	
$Co(P(O.iPr)_3)_3$	1	287	287	

TABLE 1.1 (contd.)

Lewis Acid	Stoichio-metry	Spectro-scopic	Reactivity	Other
$Rh(Ph_3P)_2X^1X^2$, X^1=Cl,Br;X^2=CN,I	1		220	
$Rh(NH_3)_5Cl_3$	1	66		
	-	65	86	
$RhCl_3$	3		221	
$RhCl_3+R_2P(O)H$	-		222	
$RhCl_2$	2		223	
RhCl	2	224	224	
$RhClH_2(PPh_3)_2$	1		288	
$\{Rh(L\text{-}L)_2\}^+PF_6^-$, L-L=bipy,phen	-	225	225	226
$RhCl(Ph_3P)_3$	-		227,228	
$\{Rh(CH\ -CH_2)_2\}_2\mu{=}Cl_2$	-		229	
RhCp	1	230	230	
$RhCp(Ph_3P)_3$	1	230	230	
$RhCl(PF_3)_2$	1	231	231	
Rh(IND)	2	232	232	
$RhCp(CH_2{=}CH_2)$	1	233	233	
$Ir(CH_2CH_2CN)CO(Ph_3P)_2$	1	84		
$IrX(CO)(Ph_3P)_2$, X=Cl,F,NCS,NCO	1	69,234,235	69	
$IrX(CO)(Ph_3P)$	1	236		
$(Ir.L\text{-}L.COD)^+PF_6^-$ L-L=bipy,phen	1	237	237	226
NiX_2, X= Cl,Br,I	2	238,239,240		

TABLE 1.1 (contd.)

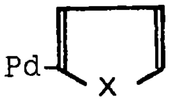
Lewis Acid	Stoichio-metry	Spectro-scopic	Reactivity	Other
$NiCl_2$	1.1,2.2,3	49	49	
$Ni(SbCl_6)_2$	6	291	291	
$Ni(InCl_4)_2$	3	291	291	
NiI_2	4	238,239,240		
$NiI_2 \cdot 4H_2O$	2	238		
$Ni(CN)_2$	Intercalate	241		
$Ni(NO_3)_2$	-			131
NiR_2bipy		242,243	242	244
$Ni(acac)_2{+}C_6H_{11}NC$	-		109	
Ni	2	28,29,36, 245	36,118,120 121,125,246, 247,248,249 250,251	38,39, 252,253
$Ni(Ph_3P)_n$, n=1,2	2	29,37	13,29,124	38
Nibipy	2			254
	1	242	242	244
$Ni\{P(O\text{-}o\text{-}tolyl)_3\}_2$	1	21,71,72	30,220,255 282	
	-			70
$Ni(CO)_4$	-		256,257	
$PdCl_2$	-		258	
 X=O,S	-		259	
$Pd(Ph_3P)_2(OAC)_2$	-		260	
$PdBrR(PR_3')_2$	-		289	

TABLE 1.1 (contd.)

Lewis Acid	Stoichiometry	Spectroscopic	Reactivity	Other
$Pd(Ph_3P)_2$	1			261
Pd(bipy)	1	262	262	
$PtCl_2$	2	263	264	
$PtCl_2.C_7H_{11}$	1	265		
PtCl(OH)	1.5	264	264	
$PtCl_2$(TMA)	1	283		
$Pt(CH_2{=}CH_2)Cl_2L$, $L{=}Et_2NH,Ph_3P$	-		130	
$Pt(Me)Me_2PhP^{3+}$	1	270		
$Pt(Ph_3P)_2$	1	35,266,267		261
PtMeHB(pyz)	1,	268,269		
$PtCF_3PMe_2Ph$	1	271		
GROUP IB				
$CuCl_2$	1	40	40	
$(CuCl_2)_2$	1	47,49	49	
$CuCl_2+CCl_4$	-		171,272	
$Cu(acac)_2+C_6H_{11}NC$	-		109,273	
Cu_2Cl_2	2	139		
	1	32	32	
$(CuCF_3CO_3)_2$	1,2	286	286	
$CuBF_4$	4		274	
$CuSnCl_3$	1	91	91	
$CuClO_4$	2	285	285	
$AgNO_3$	-	275		276
$ZnCl_2$	2	47,49,277	49,126	
	1	53,277		129
	-		278	127,128, 131,279

TABLE 1.1 (contd.)

Lewis Acid	Stoichiometry	Spectroscopic	Reactivity	Other
$Zn(SbCl_6)_2$	6	291	291	
$Zn(InCl_4)_2$	3	291	291	
ZnX_2+R_3N $X=CF_3CO_2,NCCH_2CO_2^-$ *p*-tolylSO_3^-		103,105,107		
$CdCl_2$	2	47	47	
CdX_2+R_3N $X= CF_3CO_2^-,NCCH_2CO_2^-$ *p*-tolylSO_3^-	-		103	

1.2 X-Ray Crystallographic Studies of Acrylonitrile Adducts

The possible modes of coordination of acrylonitrile (ACN) to a Lewis acid are best illustrated by consideration of the compounds that are well established and have been the subject of X-ray structure determinations. The structures fall into the categories: π bonding through the C=C double bond, and on σ bonding through the C≡N lone pair and finally a combination of both previous modes with ACN in a bridging role.

1.2.1 Acrylonitrile bonded via the C=C double bond

The reaction of $Fe(CO)_5$ with ACN yields 3 products: $\pi ACN.Fe(CO)_4$, $\sigma ACNFe(CO)_4$ and $\mu (ACN)_2(Fe(CO)_3)_2$.[19] The adduct $\pi ACN\ Fe(CO)_4$ has been shown to have a trigonal bipyramidal coordination about iron with the ACN molecule in the equatorial plane[20] (Figure 1.1). The molecular structure is monomeric, all intermolecular distances being greater than 350pm, giving the compound a high volatility. The major distortion from an ideal geometry is the bending of the N≡C-C=C plane of the ACN molecule by 13.6° from the O(2)-Fe-O(4) major axis of the trigonal bipyramid. This presumably reduces the steric repulsions between the nitrile group and the carbonyl group although this must be at the expense of reduced orbital overlap between iron d orbitals and the C=C π system.

The ethylene and ACN adducts of bis(triortho-tolylphosphite) nickel 0, $LNi[P(Oo\text{-}tolyl)_3]_2$ show similar structures [21] (Figures 2 and 3) to $\pi ACNFe(CO)_4$. Comparison of the ethylene and ACN structures enables a discussion of the metal olefin bond in terms of steric and electronic effects.

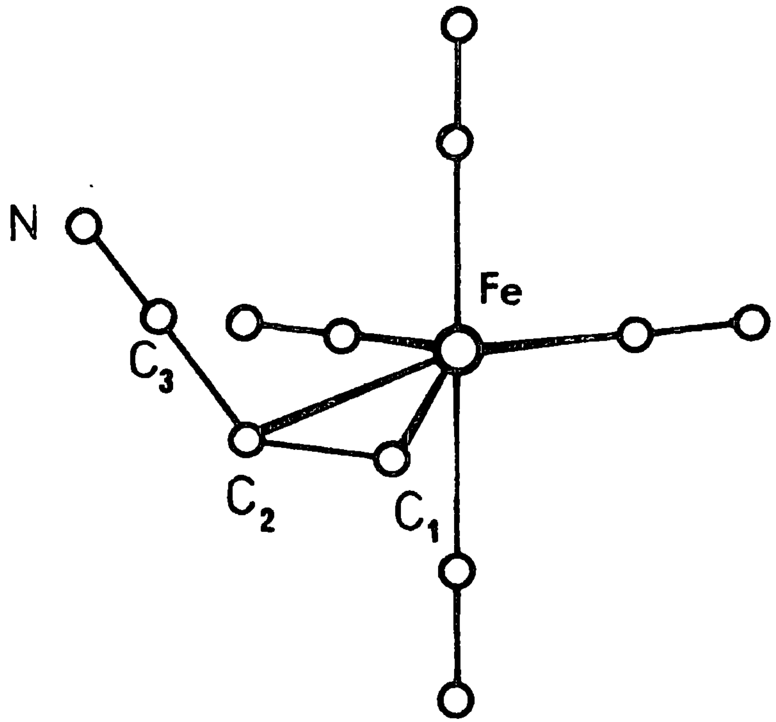


Figure 1.1. Molecular Structure of ACN.$Fe(CO)_4$

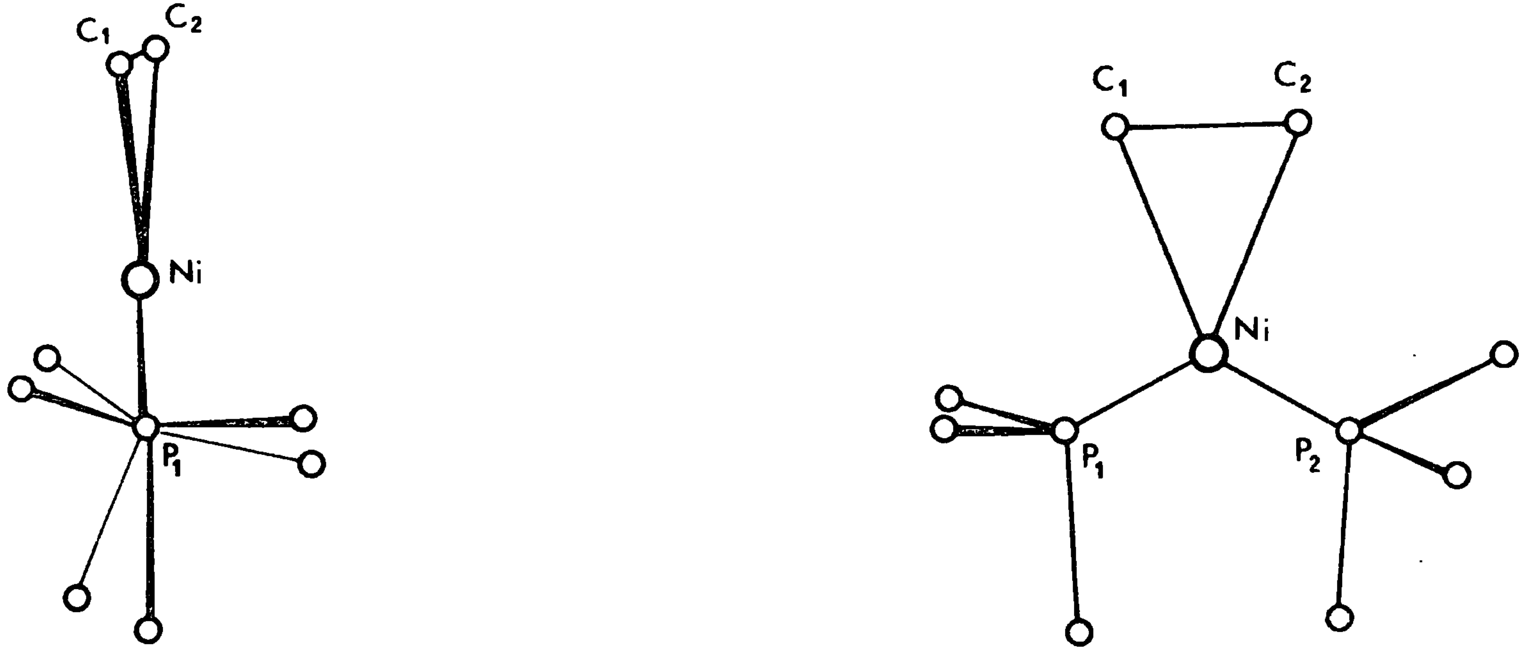


Figure 1.2. Molecular Structure of $(C_2H_4).Ni[(o\text{-}CH_3C_6H_4O)_3P]_2$

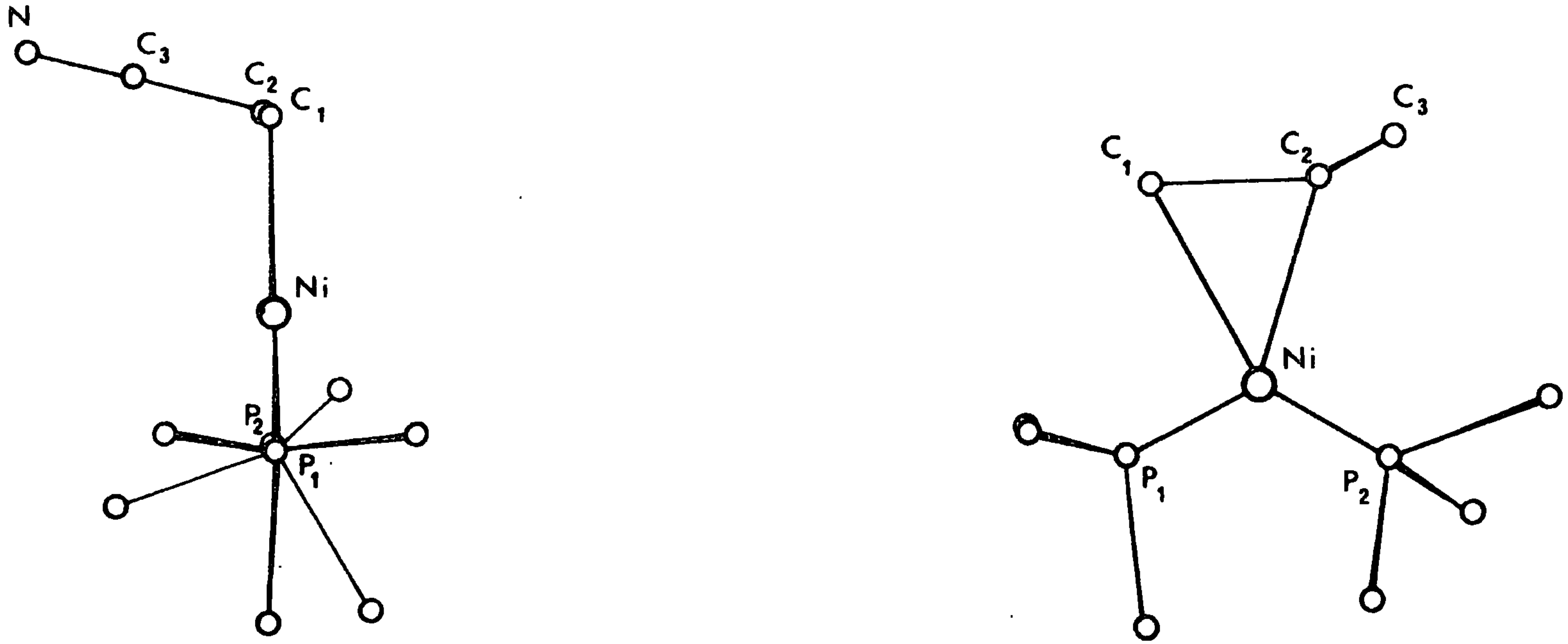


Figure 1.3 Molecular Structure of ACN.Ni[(o-$CH_3C_6H_4O)_3P]_2$

The ACN causes considerable distortion in all three planes. In the ethylene adduct the tritolylphosphite ligands adopt a near ideal, eclipsed position (Figure 1.2) whereas the presence of the CN group in the ACN adduct causes a staggered conformation to be adopted. The steric effect of the nitrile group also causes the plane of the ACN molecule to be bent away from the normal of the C-Ni-C plane by 13.2° in a similar fashion to $\pi ACNFe(CO)_4$. Also in the ethylene complex the C-Ni-C plane is twisted by 6° out of the P-Ni-P plane. In contrast in the ACN adduct the planes are folded by 4°. This again is most probably a steric distortion.

The most significant effects of the nitrile group are however electronic in origin. The Ni-C bonds in the acrylonitrile adduct are some 5pm shorter than in the ethylene adduct and the ACN molecule is displaced along the C=C axis so as to bring the nitrile end of the molecule nearer the nickel atom. Guggenberger[21] considers these electronic effects, the former being caused by the stabilization of the olefinic π^* orbital by the CN group causing greater $Ni(d) \longrightarrow C{=}C(\pi^*)$ donation leading to a shorter Ni-C bond length. This σ donation, π back donation formalism of Dewar,[22] Chatt and Duncanson[23] will be discussed later (see page 26).

1.2.2 Adducts bonded through the nitrogen of acrylonitrile

Prior to this work no compounds containing solely N bonded acrylonitrile had been the subject of a structure determination.

In this thesis (Chapter Two) we will report the structure of the N bonded adduct hexakisacrylonitrile nickel II hexachlorodizincate.

1.2.3 Adducts containing bridging Acrylonitrile

The rigid stereochemistry of the acrylonitrile molecule precludes coordination of the nitrile and the C=C double bond to the same centre. Acrylonitrile may however adopt a bridging role and has been crystallographically observed in $Cu_2Cl_2.\mu ACN$,[24] $Mo_2(CO)_4(PBu_3)_4(\mu ACN)_2$ and proposed to exist $(Fe(CO)_3)_2(\mu ACN)_2$.[26] The molybdenum complex (Figure 1.4) is a dimeric $Mo(CO)_2.(PBu_3)_2$ unit linked by two ACN groups. Like the 2 pure π complexes discussed above the nitrile group is bent out of the C-Mo-C plane but by 23° compared with 13° in the other adducts. This must be not only due to the steric effect of the nitrile group but a distortion necessary for the formation of the dimeric molecule, the loss of stability due to reduced Mo(d),C=C(π) orbital overlap being compensated for by the formation of the N-Mo bond.

The second example of ACN in a bridging role involves ACN coordinating to chemically different centres. The adduct Cu_2Cl_2.ACN contains the units Cu(1)Cl_2.olefin and Cu(2)Cl_3 nitrile (Figure 1.5). The first unit contains Cu(1) in a pseudotrigonal coordination sphere bonded to two chlorine atoms and the C=C double bond of acrylonitrile. The trigonal plane is slightly distorted due to a third chlorine at 272pm in a second coordination sphere. The second copper atom (Cu(2)) is tetrahedrally coordinate, surrounded by three chlorines and the nitrile group of ACN. The two units are then linked by chlorine bridges and the ACN backbone. In contrast to the molybdenum dimer above the acrylonitrile plane is not significantly bent from the normal to the C-Cu-C plane since the geometry about Cu, enforced by the dimeric units, is nearly ideal.

FIGURE 1.4 Molecular structure of $Mo_2(CO)_4(PBu_3)_4(\mu ACN)_2$

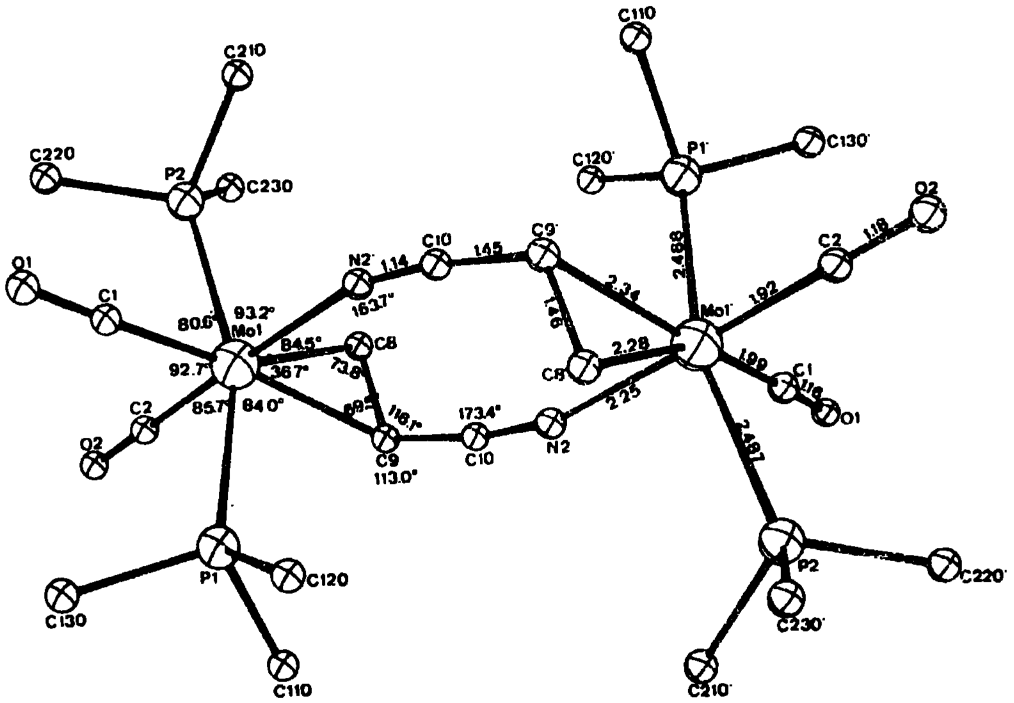
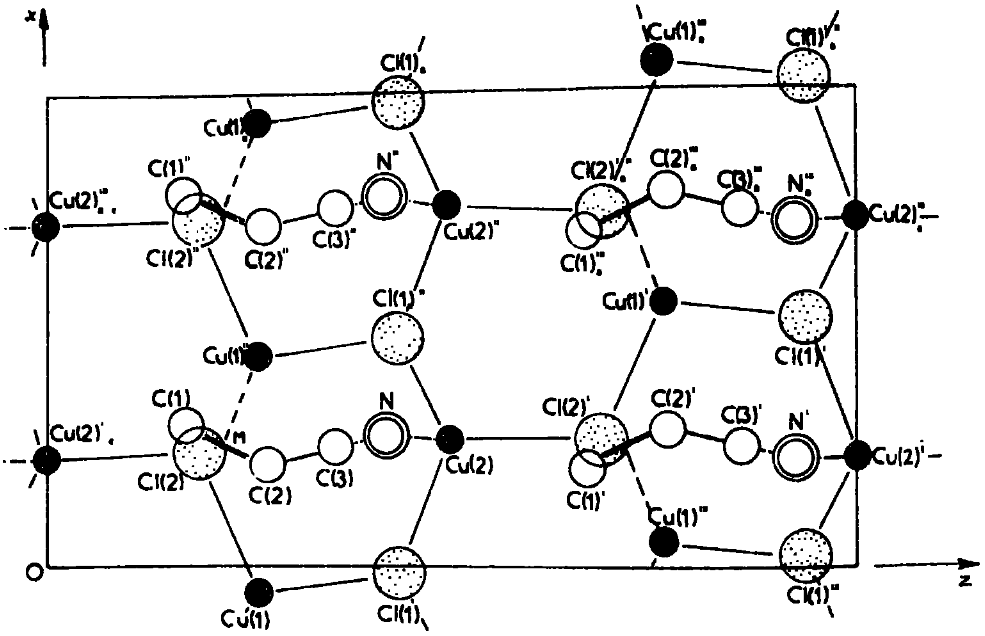
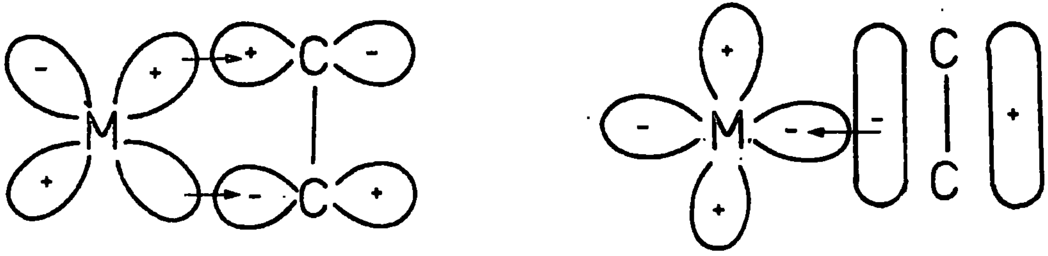


FIGURE 1.5 Unit Cell of $Cu_2Cl_2\mu ACN$ projected on Y axis



In all the structures discussed above the effect of coordination of acrylonitrile through the C=C double bond is to lengthen the double bond (Table 1.2). The degree of lengthening is representative of the reduction in bond order due to both donation of electron density from the HOMO(π) of ACN to the d orbitals of the metal and back donation from metal d orbitals into the LUMO(π^*) of ACN (Figure 1.6).

The effect of π coordination through the C=C double bond on the C≡N triple bond is unclear due to the size of the standard deviations in the CN bond lengths. Coordination of the nitrile group by σ donation of the lone pair on nitrogen to metal d orbitals and back donation from d orbitals into the π^* system of the nitrile should cause lengthening of the CN bond. However no such lengthening is observed in the ACN adducts (Table 1.2) which does not fall within the standard deviations. Further treatment of the effect of coordination of the CN group will be left until section 1.3 where the vibrational spectra of coordinated nitriles will be discussed.



$d \longrightarrow \pi^*$ $\qquad$ $\pi \longrightarrow d$

Figure 1.6

TABLE 1.2 Bond Lengths (pm) in Acrylonitrile Adducts

Compound	M - C_1*	M - C_2*	$C_1 = C_2$	C≡N
Free ACN	-	-	133.9(1)	116.4(1)
Fe(CO)$_4$.ACN	210(10)	209(16)	140(22)	120(22)
Ni(P(O o tolyl))$_2$.ACN	201.6(10)	191.1(12)	146(2)	120(2)
Cu_2Cl_2.ACN	207.3(12)	204.3(12)	138.4(20)	115.4(6)
$Mo_2(CO)_4(PBu_3)_4$ (μACN)$_2$	235.1(8)	228.3(8)	146(1)	114(1)
Ni(ACN)$_6$Zn$_2$Cl$_6$	206(5)†		127(7)	113(5)

* Metal olefin distances

† Metal nitrogen distance

1.3 Spectroscopic Studies of Acrylonitrile Adducts

Whilst a few ACN adducts have been the subject of X-ray crystallographic studies the mode of bonding in ACN adducts has usually been determined from spectroscopic data such as infra-red, Raman and nuclear magnetic resonance spectra. As illustrated in section 1.2, ACN is known to bond via the C=C double bond, side on, and the CN triple bond, end on, by donation of the lone pair on nitrogen. In principle it may also bond side on via the nitrile group analogous to acetylene complexes. No side on nitrile complexes of ACN have been proposed however and the reason for this may be seen from consideration of the molecular orbital coefficients of the highest occupied molecular orbital, Ψ_2, (HOMO) and the lowest unoccupied molecular orbital, Ψ_3, (LUMO) of ACN[28] (Figure 1.7).

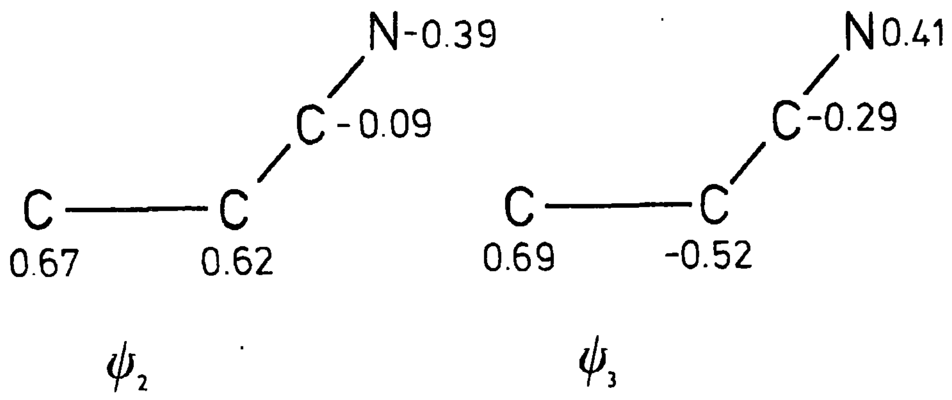


Figure 1.7.

The molecular orbital coefficients are largest on the olefinic carbons in both the HOMO and LUMO leading to good overlap at the C=C double bond both for donation of electron density from the HOMO to the metal d orbitals and also for back donation from the metal d orbitals to the LUMO. Thus side on bonding via the nitrile group is not to be expected.

1.3.1 Adducts proposed to contain ACN bonded via the double bond

The effect of coordination via the C=C double bond on the infra-red spectrum of ACN is illustrated in Table 1.3. The most important effect is that ν(C=C) at 1608 cm^{-1} in free ACN invariably drops by at least 90 cm^{-1} due to reduction of the C=C bond order as discussed in section 1.2.

Considerable interest has been focused on the compound $Ni^{\underline{0}}$.2ACN from the point of view of bonding implications to other π complexes and its catalytic activity in cycloaddition and related reactions (see section 1.5.3). It may be prepared simply by refluxing ACN with $Ni(CO)_4$.[36] Addition of triphenylphosphine yields the mono- or bisphosphine bis(ACN)nickel complexes[37,38] and on this basis and the infra-red spectra, a π bonded structure was deduced. Unfortunately the crystal of the compound has not been determined.

In addition to the changes in ν(C=C) in the infra-red spectra a number of other modifications of the vibrational spectra occur. The bands due to the methylene twist and wag $\tau(CH_2)$ and $\omega(CH_2)$ shift to lower frequency. The shift in $\nu(C{\equiv}N)$ may be zero or negative and is a function of the back donation of electronic charge from the metal into

TABLE 1.3 Infra-red Frequencies (cm^{-1}) of ACN Adducts Bonded via the C=C Double Bond

Lewis Acid	Stoichiometry	$\nu(C\equiv N)$	$\Delta\nu(C\equiv N)$	$\nu(C=C)$	Ref
Free ACN	-	2230	-	1608	-
$Ni(P(O\ otolyl)_3)_2$	1	2194	-36	?	30
$Fe(CO)_4$	1	2226	-4	?	31
Cu_2Cl_2	1	2217	-13	1502	32
$Mo_2(CO)_2(PBu_3)_4$	2	2219,2212	-11,-18	1595	25
Ni	1	2220	-10	1446	29
$Ni(Ph_3P)$	1	2191	-39	?	29
$Ni(Ph_3P)_2$	1	2175	-55	?	29
$Pt(PPh_3)_2$	1	2195	-35	?	35
$W(CO)_3$	3	2221	-9	1440	33
$Mo(CO)_3$	3	2225	-5	1456	34
$CrMe_3C_6H_3(CO)_2$	1	2197	-33	?	54
$CrMe_6C_6(CO)_2$	1	2195	-35	?	54

the π^* orbitals. This is illustrated by the series of adducts $(PPh_3)_n$Ni2ACN n = 0,1,2. When n=0 the nickel is a poor donor of electron density and $\Delta\nu(C\equiv N)$ is small. However when good electron donating ligands such as phosphines are bonded to nickel the additional electron density offloaded to the Ni2ACN unit causes $\nu(C\equiv N)$ to drop by 39 cm^{-1} when one phosphine is bonded and by a further 16 cm^{-1} when two phosphines are present (Table 1.3). Also with greater back donation the C=C bond order is further reduced and $\nu(C=C)$ drops into the region where C-C single bond stretching frequency occurs.

Several π complexes have been prepared as models for the structure and bonding is bis(ACN)nickel. The copper I halide π adducts were prepared[39,40] and Cu_2Cl_2.ACN was later shown to contain bridging ACN. The ACN and acrolein adducts of $Mo_2(CO)_2L$ are believed to be polymeric with bridging ACN units [41,42] (Figure 1.8a) and are possible models for bis(ACN)$Ni^{\underline{o}}$ (Figure 1.8b). This model would be consistent with the uptake of two molecules of phosphine whilst maintaining maximum coordination about the nickel atom.

Numerous other π bonded adducts of ACN have been isolated and characterized. The photolysis of $Fe(CO)_5$ in non-polar solvents yields both N and π bonded isomers of ACNFe$(CO)_4$ and an adduct $Fe(CO)_3$.ACN which is formulated as the bridged dimer $(Fe(CO)_3)_2$ $(\mu ACN)_2$ on the basis of the carbonyl vibrational frequencies, nmr data[19] and a preliminary crystallographic study.[26]

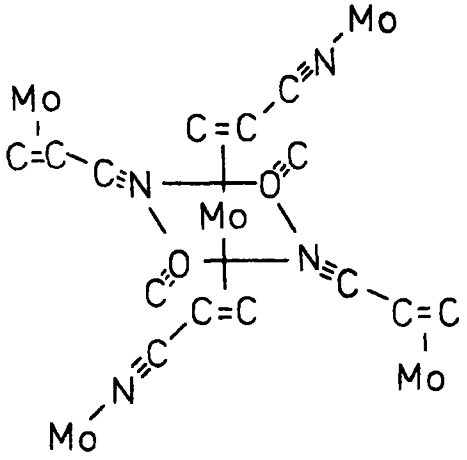


Figure 1.8.a.

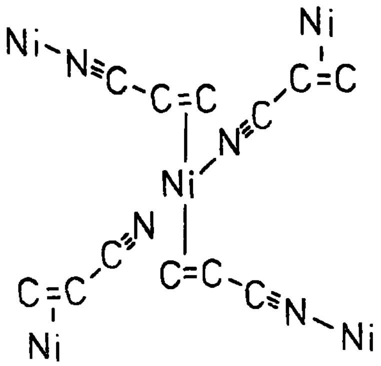


Figure 1.8.b.

1.3.2 Adducts proposed to contain Acrylonitrile bonded via nitrogen

The nitrile group of ACN will behave in a similar manner to other simple nitriles. The nitrile group is an essentially pointed ligand with the substituent sterically unimportant in the first coordination sphere. There are a great many well established examples of N bonded acrylonitrile adducts with hard Lewis acids (Table 1.1) such as the octahedral adducts MX_5,ACN where M=Ta,Nb[43,44], Sb[45], MCl_4,2ACN where M=Ti,Ta,Zr,Nb[43,44], Sn[46], MX_3.3ACN where M=V,Ti[43,44], Cr[47], Mo[48] and the tetrahedral adducts MCl_2,2ACN where

M=Fe,Mn,Co[47,49]. Analysis of the far infra-red and Raman spectra show that the tetrahalide adducts have a *cis* stereochemistry and MX_3.3ACN M=V,Ti have a *mer* octahedral coordination.[43,44]

Many metal salts undergo solvolysis in acrylonitrile by analogy with metal salts in acetonitrile. Aluminium trichloride is known to give ionic solutions containing $Al(ACN)_6^{3+}$ and $AlCl_4^-$ species from ^{27}Al and ^1H nmr studies[50] although the validity of such claims regarding the nature of the solvated species must be carefully examined in the light of a comprehensive study of the MeCN-$AlCl_3$ system.[51] Studied by ^1H, ^{27}Al nmr, infra-red and Raman spectroscopy, conductivity and X-ray crystallography the results show that the crystalline product $AlCl_3$,2MeCN isolated from MeCN solution has the structure $[AlCl(MeCN)_5]^{2+}$ $[AlCl_4^-]_2$.MeCN.

Similarly a mixture of $ZnCl_2$ and $NiCl_2$ (from the reaction of $NiCl_2$ and Zn dust) undergoes solvolysis[49,52] in MeCN to give $Ni(MeCN)_6^{2+}$ $ZnCl_4^{2-}$. Our own work shows that a similar reaction occurs in ACN or propionitrile but yielding NiL_6^{2+} $Zn_2Cl_6^{2-}$ (Chapter Two).

The effect of coordination of the nitrile function on the infra-red spectra is summarized in Table 1.4. The absorption frequency of a nitrile group generally increases upon coordination to an electron deficient centre. If the bonding of the nitrile can be represented by Figure 1.9 by analogy with the bonding scheme in metal carbonyls then a decrease in $\nu(C\equiv N)$ is to be expected due to the increased population of the π^* orbitals reducing the bond order. However a decrease in $\nu(C\equiv N)$ is <u>not</u> the general observation[5].

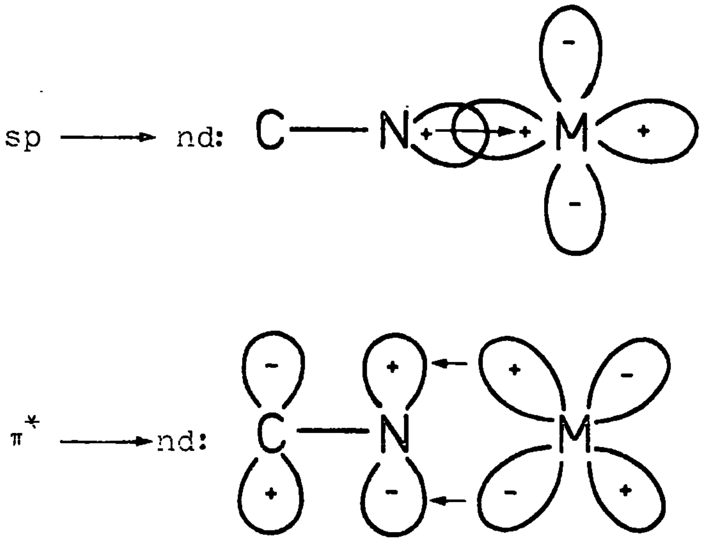


Figure 1.9.

Possible reasons for this are an increase in the C≡N force constant due to increased C≡N σ bond strength and/or kinematic coupling between the N —— acid bond and the C≡N bond. Purcell and Drago[55,56] calculated the effect of varying the adduct bond force constant and the Lewis acid mass on ν(C≡N) by a force constant analysis in a number of BX_3.MeCN adducts. They found that acid masses of greater than 10 all have the same effect on the CN stretching frequency implying that the adduct force constant cannot explain all the changes in ν(C≡N) as adduct force constants are known to lie between 0.9 mdy/Å (Zn^{2+}) and 2.5 mdyn/Å (BF_3.MeCN). Thus kinematic coupling only accounts for 10 cm^{-1} shift in $ZnCl_2$.2MeCN and 50 cm^{-1} in BF_3.MeCN.

On calculating the overlap energies of the atomic orbital pairs in the CN bond in the free and coordinated nitrile they found that the most important stabilizing effect on coordination was the drop in energy of the N_s orbital in the N_s-C_s and N_s-$C_{p\pi}$ molecular orbitals. Changes in the $N_{p\pi}$=$C_{p\pi}$ overlaps were negligible. In simple bonding terms this implies that coordination entails the donation of the lone pair from an orbital which has greater p character than a normal sp hybrid orbital and the CN σ bond contains an MO to which nitrogen contributes an s character biased sp hybrid. The net effect of this stabilization of the C≡N bond is shown in the molecular orbital diagram in Figure 1.10

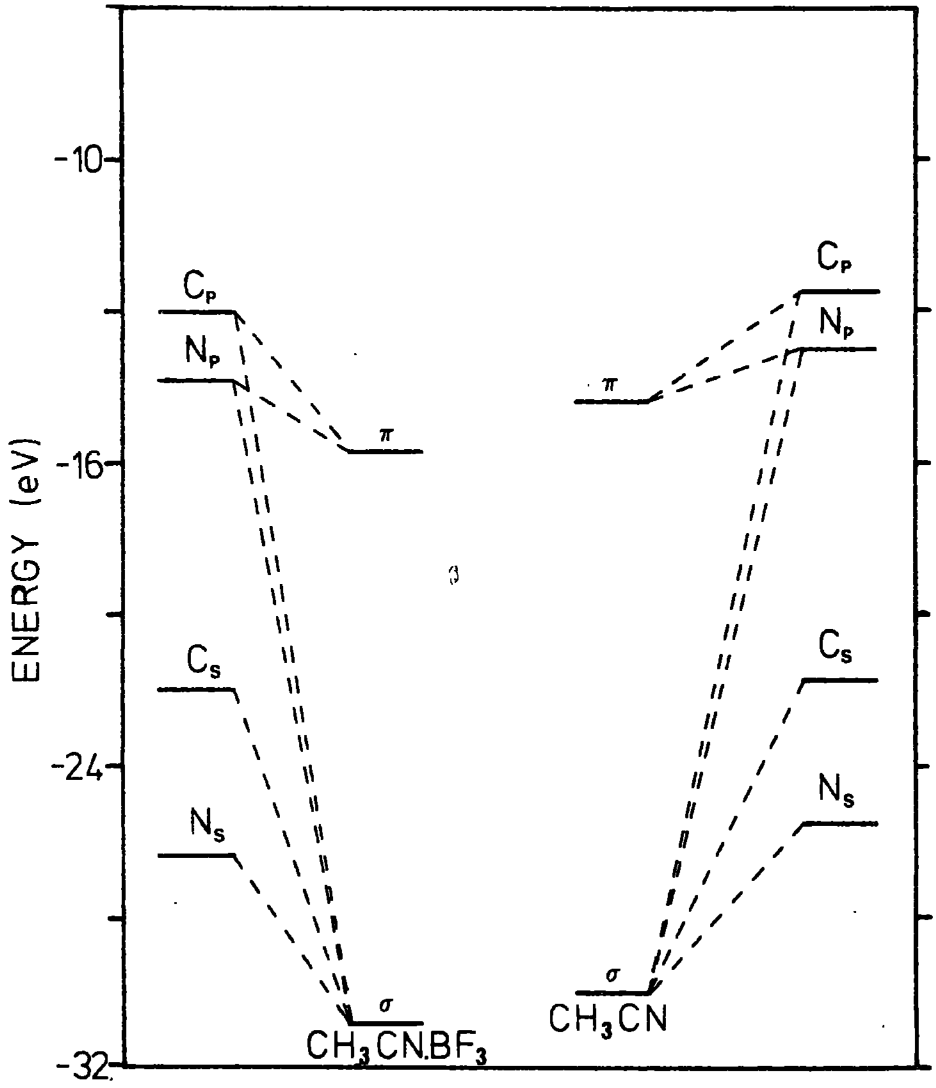


Figure 1.10

In a high accuracy crystallographic study these increases were confirmed in the adducts $BX_3.MeCN$ (X=Cl,F).[57,58] Increases in ν(CN) were found to be accompanied by a reduction in the CN distance from 115.7pm to 113.5pm for X=F and 112.2pm for X=Cl representing an increase in the force constant from 17.4 mdyn/Å to 18.8 mdyn/Å and 18.7 mdyn/Å respectively. The BX_3.ACN adducts may be assumed to undergo a similar change.[60] Changes in the C≡N force constant may be estimated by making a few assumptions about the structure. For instance if the adduct $ZnCl_2$.ACN is assumed to have a Zn-N distance of 200pm thus a Urey-Bradley force field calculation[61] predicts an increase in the CN force constant from 16.7 mdyn/Å to 17.6 mdyn/Å if only Zn-ACN vibrations are considered or 17.3 mdyn/Å if the structure is regarded as a chlorine bridged dimer (Zn-Cl = 240pm).

The nitrile stretching frequency may only be lower than the free nitrile when donation from metal d orbitals into the π^* orbitals of the CN group more than offsets the CN bond strengthening due to N coordination. This may be observed in the series $Cr(CO)_2$.L.ACN (Table 1.4). When the electron donating power of the ligand increases in the order $CO < 1,4(MeCO_2)_2C_6H_4 < C_6H_6$, and ν(CN) is found to steadily decrease in that order[54]. However when L=1,3,5 $Me_3C_6H_3$ and C_6Me_6 the nmr indicates that the acrylonitrile becomes bonded via the C=C double bond. Evidence of C=C bonding, in addition to vibrational spectra, is highly desirable since ν(C=C) may be weak or obscured in an adduct and a π bonded structure wrongly inferred. Similarly caution must be employed when inferring similar structures from similar formulae. For instance Δν(C≡N) in $RuCl_2(PPh_3)_2$.2ACN.[62] and $Ru(NH_3)_5.ACN^{2+}$

TABLE 1.4 Infra-red Frequencies (cm^{-1}) of N bonded ACN Adducts

Lewis Acid	Stoichiometry	$\nu(C\equiv N)$	$\Delta\nu(C\equiv N)$	$\tau(CH_2)$	$w(CH_2)$	$\nu(C=C)$	Ref.
Free ACN	-	2230	-	975	975	1608	-
$TiCl_4$	2	2275	+45	964	990	1603	53
$SnCl_4$	2	2255	+25	947	978	1595	47,53
$AlCl_3$	1	2291	+61	958	993	-	53
$AlEt_3$	1	2276	+46	963	989	-	53
$ZnCl_2$	2	2280	+50	962	994	1602	47,53
$MnCl_2$	1	2252	+22	962	975	1603	47
$FeCl_2$	1	2257	+25	961	975	1600	47
$CrCl_3$	3	2268	+38	972	999	1600	47
$W(CO)_5$	1	2244	+14	-	-	-	54
$Cr(CO)_5$	1	2252	+32	-	-	-	54
$1,4(MeCO_2)_2C_6H_4Cr(CO)_2$	1	2227	-3	-	-	-	54
$C_6H_6Cr(CO)_2$	1	2197	-33	-	-	-	54

are negative. However nmr indicates the former to be a π bonded structure whilst in the latter the α hydrogen is deshielded by 0.25ppm and the terminal hydrogens appear upfield from free ACN[63,64]. The deshielding of the α proton is due to interaction with the cation whilst the terminal hydrogens are shielded due to strong back donation into the π^* orbitals suggesting an N bonded adduct. In contrast Isoelectronic Rhodium III adducts[65,66] show positive $\Delta\nu$ (C≡N) because Rh^{III} is a stronger Lewis acid accommodating more electronic charge. This is because the additional t_{2g} electron does not effectively shield the additional nuclear charge and the incomplete $4d^5$ configuration of Ru^{II} allows for better pπ-dπ interaction than the $4d^6$ configuration of Rh^{III}.

A second effect of C≡N coordination on the infra-red spectra of ACN is to split the vinyl twist and wag frequencies which are exactly superimposed in ACN at 968 cm^{-1}. This is due to the increase, on coordination, of the inductive effect of the nitrile giving rise to bonding contribution from structure shown in Figure 1.11. In $SnCl_4$.2ACN the bond splits to 947 cm^{-1} and 978 cm^{-1}. Since a more electropositive metal centre will give rise to a more inductive

$$^{+}CH_2{-}CH{=}C{=}N{-}MX_n^{-}$$

Figure 1.11

nitrile group the methylene twist frequency is expected to drop and the wag to increase.[47,61] The amount of splitting thus provides a useful direct measure of relative Lewis acidity.[53]

1.4 Ligand Properties of Acrylonitrile

1.4.1 Comparitive Studies with nitriles

The nitrile function is generally insensitive to the steric effects of the substituent (see above and Chapter Four). The most important factor influencing the relative stabilities of nitrile adducts is the electronic nature of the substituent.

Electron withdrawing substituents on the nitrile reduce the stability of the adducts by reducing the donating power of the nitrile and vice versa. The vinyl group seems to be relatively neutral in this respect. The ^{121}Sb Moessbauer spectra[65] and the vibrational spectra[45] indicate that the $SbCl_5.ACN$ adducts have stabilities in the order $CCl_3 < CH_2Cl < CH_2CH \approx Et \approx Bu^t < NC(CH_2)_3 \approx Ph \approx NC(CH_2)_4$. A similar ordering is obtained when one compares the stability constants for the equilibrium:

$$MCl_5.RCN + R'CN \rightleftharpoons MCl_5.R'CN + RCN \qquad M = Ta,Nb$$

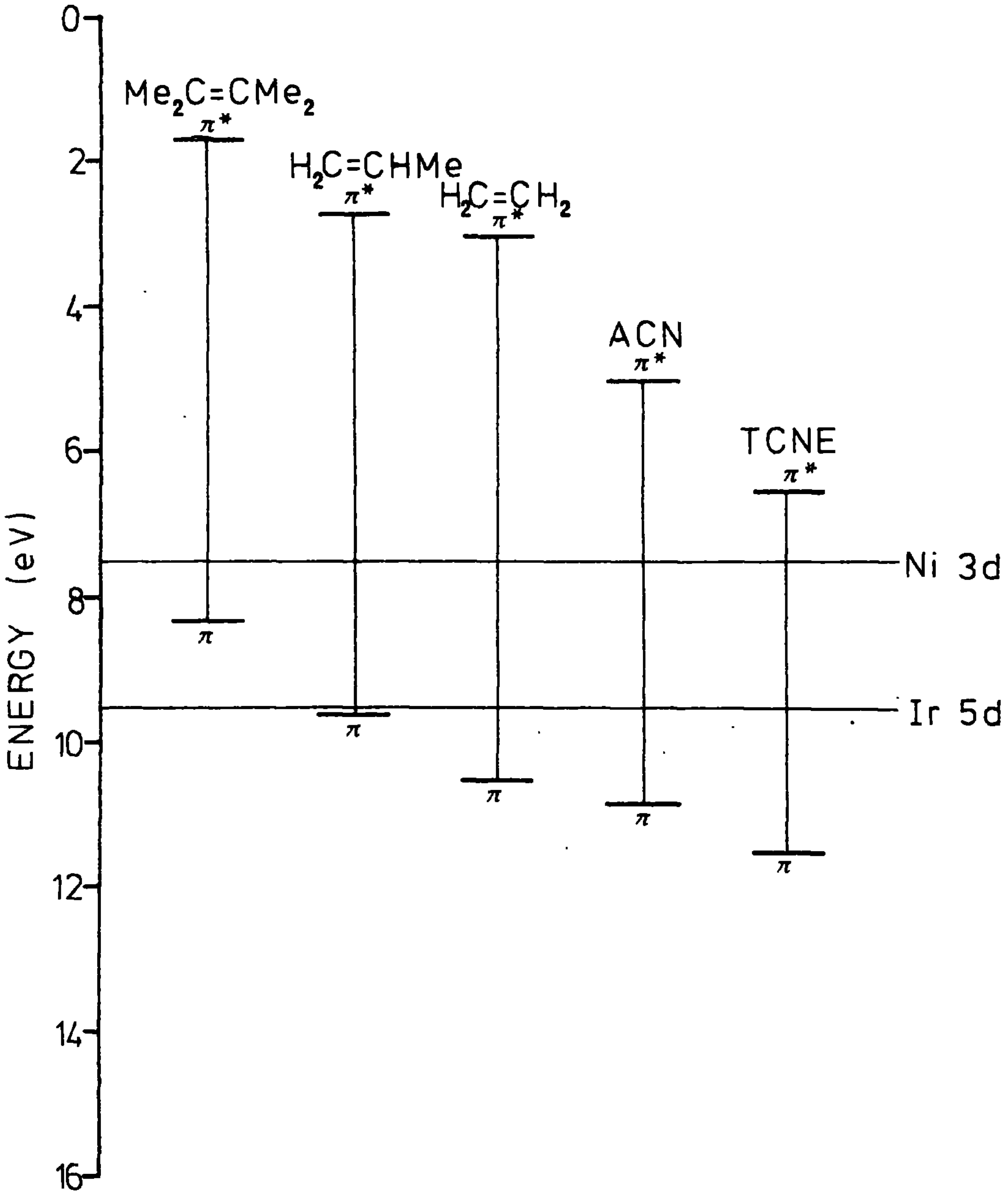
The equilibrium constant is found to increase in the order $FCH_2CN < ClCH_2CN < BrCH_2CN < ICH_2CN \ll ClC_6H_4CN \approx CH_2CHCN < C_6H_5CN < MeCN \approx Bu^tCN$. However care should be taken when comparing results obtained by such widely different methods especially in view of the divergent ideas of what is meant by the term 'stability'. Further discussion of the relative stability of acrylonitrile adducts compared with other good σ donors will be found in Chapters Two, Three and Four.

1.4.2 Comparitive Studies with Olefins

The cyano-olefin complexes $IrX(CO)(Ph_3P)_2.L$ (X=Cl,Br,I,NCS,NCO) were found to have stabilities in the order tetracyanoethylene (TCNE) > Fumaronitrile (FMN) >> ACN from observations of ligand displacement reactions, vapour pressure measurements and carbonyl stretching frequency increases (+100,70,62 cm^{-1} respectively).[69] (No adducts could be isolated with cinnamonitrile, crotonitrile or diphenylmethylene malononitrile). The changes in $\nu(CO)$ indicate that more electronic charge is being donated into the olefin π^* orbitals from the metal thus reducing the extent of metal d to carbonyl π^* transfer and increasing $\nu(CO)$. A similar sequence of stability is found for the (olefin)Ni($P(O\,o\text{-}tolyl)_3)_2$ complexes: maleic anhydride > FMN > ACN ≈ dimethyl maleate > methyl acrylate > ethylene.[70,71,72]

These results may be rationalized on the basis that electron withdrawing substituents improve the π acceptor power of the olefin. This is shown by consideration of the energy levels of the orbitals used in olefin to metal donation and metal to olefin back donation illustrated in Figure 1.12. Olefin to metal donation is favoured by good π-d overlap which in these cases requires a high π orbital energy. However the effect of adding electron withdrawing substituents is to reduce the π energy levels and reducing the donor capacity. However this destabilization is offset by the reduction of π^* orbital energy levels because the π^* orbitals fall in energy faster than the π orbitals hence reducing the π-π^* gap from 7.9eV in ethylene to 5.7eV in ACN and 5.0eV in TCNE. Hence the effect of adding a cyano group to ethylene is to make the C=C bond a poorer donor of electrons but a far better acceptor when interacting with metal orbitals between 7.5 and 9eV.

Figure 1.12. Energy Levels of π and π^* Orbitals in some Olefins c.f. Metal d Orbitals



1.5 Reactions involving coordinated Acrylonitrile

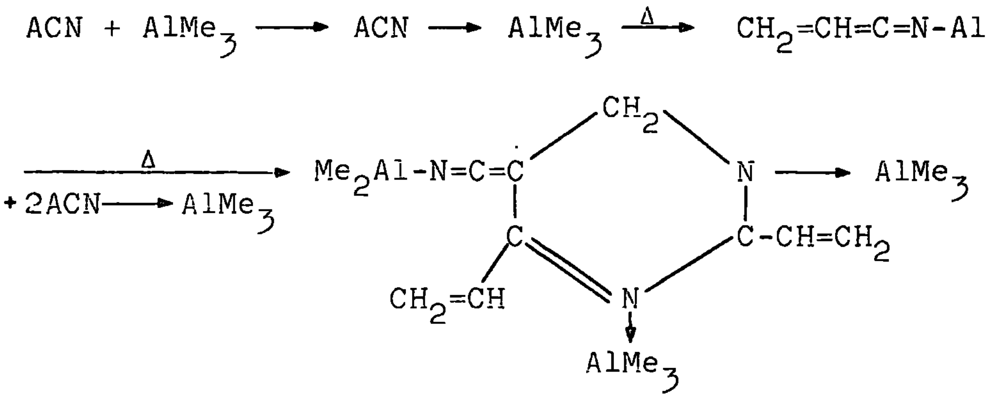
The reactions of coordinated acrylonitrile fall into two categories. The first is the reduction of one or both of the unsaturated linkages of the molecule by insertion into a metal alkyl or metal hydrogen bond. The second category is the group of reactions broadly classed as oligometizations. No discussion will be made of acrylonitrile polymerization systems since the field is extremely large and not immediately relevant to this review.

1.5.1 Reduction

The nitrile group may be reduced by a dialkyl aluminium hydride to give a vinyl imino aluminium dialkyl.[73] The free imine may be displaced by a weak acid such as acetylacetone (Equation 1.1)

$$\mathrm{ACN} + \mathrm{HAlBu_2^{\,i}} \longrightarrow \mathrm{H_2C{=}CHC{=}NAlBu_2^{\,i}} \xrightarrow[-5^{\circ}\mathrm{C}]{\mathrm{HAcAc}} \mathrm{H_2C{=}CHCH{=}NH} \qquad (1.1)$$

If trimethylaluminium is used as a reducing agent the N bonded adduct may be isolated initially.[74,75] Warming the adduct causes elimination of methane and trimerization via a heterocumulene (Equation 1.2)

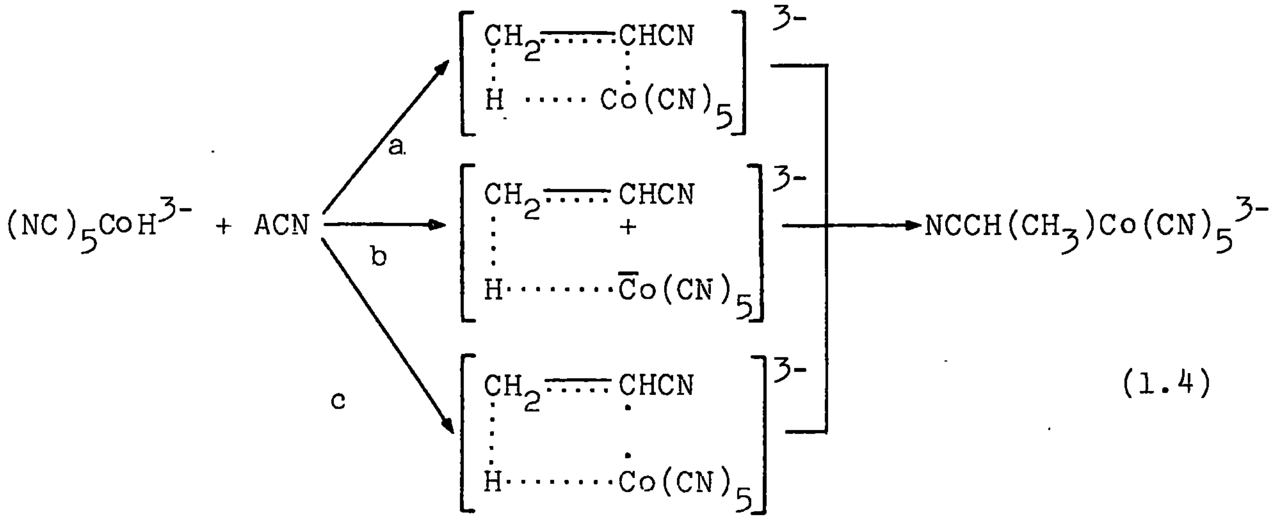


(1.2)

In contrast alkyl tin hydrides undergo 1,2 additions to the C=C double bond.[76-79] The reaction yields both the α and β metallated product[78] (equation 1.3).

$$\text{ACN} + R_3SnH \longrightarrow \underset{\alpha}{R_3SnCH(CH_3)CN} + \underset{\beta}{R_3SnCH_2CH_2CN} \qquad (1.3)$$

Addition of a free radical increases the rate of formation of the β product but has no effect on the rate of formation of the α product whereas the rate of formation of the α product increases with solvent polarity. This suggests that the β product is formed in a free radical addition of $H^{\cdot}$ and $SnR_3^{\cdot}$ whilst the α product is the result of electrophilic attack of $\overset{\delta-}{H} — \overset{\delta+}{SnR_3}$. The C=C double bond is also reduced by hydride pentacyanocobaltate III compounds giving solely the cyanoethyl pentacyanocobaltate compound.[16,17,80] The mechanism is not well established and 3 reaction schemes consistent with the data have been proposed with either (a) a 4 centre intermediate, (b) a polar intermediate or (c) a free radical intermediate (Equation 1.4).



(1.4)

A cyanoethyl cobalt species may also be prepared by the reduction of ACN with bis(dimethylglyoximato)cobalt II base complex (Figure 1.13). In neutral solution the α product predominates (equation 1.5) whilst in alkaline solution the β adduct is the major product[81] (equation 1.6).

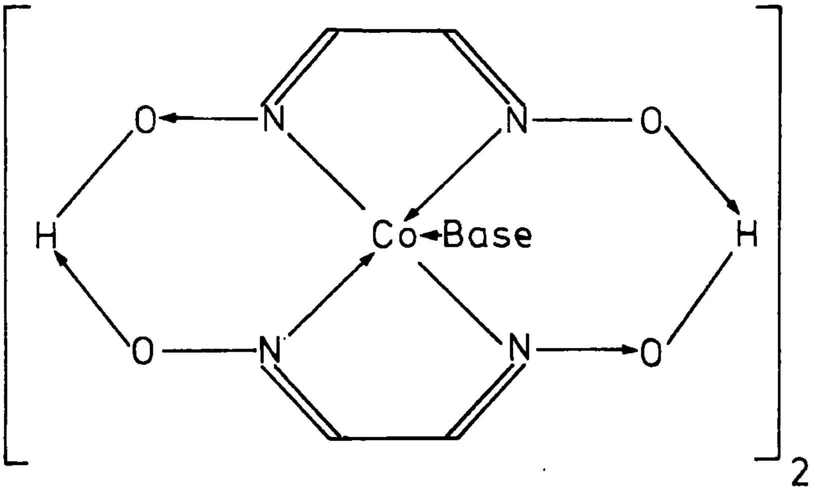
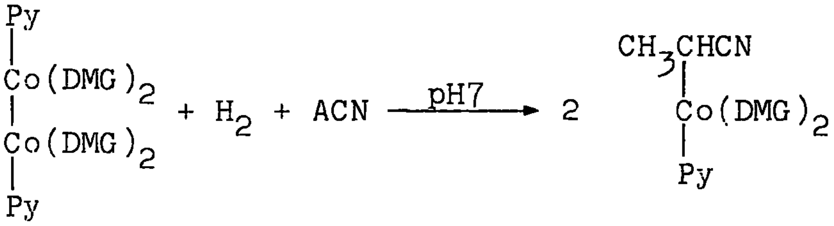
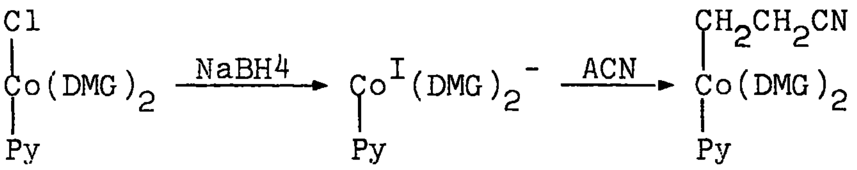


Figure 1.13

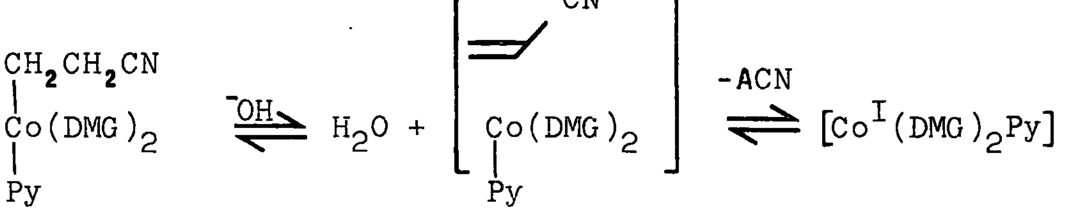


$$\mathrm{Py{-}Co(DMG)_2{-}Co(DMG)_2{-}Py} + H_2 + \mathrm{ACN} \xrightarrow{\mathrm{pH7}} 2\ \mathrm{CH_3CHCN{-}Co(DMG)_2{-}Py} \qquad (1.5)$$



$$\mathrm{Cl{-}Co(DMG)_2{-}Py} \xrightarrow{\mathrm{NaBH4}} \mathrm{Co^{I}(DMG)_2^{-}{-}Py} \xrightarrow{\mathrm{ACN}} \mathrm{CH_2CH_2CN{-}Co(DMG)_2{-}Py} \qquad (1.6)$$

In strongly alkaline conditions the β complex undergoes cobalt-carbon bond cleavage to give the π olefin complex[82] (equation 1.7)



$$\mathrm{CH_2CH_2CN{-}Co(DMG)_2{-}Py} \underset{}{\overset{^{-}OH}{\rightleftharpoons}} H_2O + \left[\mathrm{CN\ olefin{-}Co(DMG)_2{-}Py}\right]^{-} \overset{-ACN}{\rightleftharpoons} [\mathrm{Co^{I}(DMG)_2Py}]^{-} \qquad (1.7)$$

The α metallated adduct undergoes complete hydrogenation to propionitrile on the addition of cobalt catalyst.

The reactions of a number of low valent transition metal hydrides with acrylonitrile have been studied and show a variety of different pathways. Whilst cyclopentadienyl iron dicarbonyl hydride yields the α addition product with ACN[83] (equation 1.8) without isolation of an intermediate complex, the initial reaction of ACN with $IrH.CO.(Ph_3P)_3$ yields the π complex and only in the presence of excess ACN may the β cyanoethyl complex be isolated[84] (equation 1.9).

$$CpFe(CO)_2H + ACN \longrightarrow CpFe(CO)_2CH(Me)CN \qquad (1.8)$$

$$IrH(CO)(Ph_3P)_3 + ACN \xrightarrow{-Ph_3P} IrH(CO)(Ph_3P)_2.ACN$$
$$\xrightarrow[ACN]{XS} Ir(CH_2CH_2CN)(CO)(Ph_3P)_2ACN \qquad (1.9)$$

Similarly Cp_2MoH_2 will only reduce one molecule of ACN at low concentrations of olefin. Addition of excess ACN causes elimination of propionitrile and yields the π adduct[85] (equation 1.10).

$$Cp_2MoH_2 + ACN \longrightarrow Cp_2MoH(CH_2CH_2CN)$$
$$\xrightarrow{XS} Cp_2Mo\pi(CH_2CHCN) + CH_3CH_2CN \qquad (1.10)$$

Acrylonitrile may be activated towards carbonionic addition by coordination to pentammine complexes of Co^{III}, Ru^{III}, Rh^{III}. Thus catalytic addition of weak acids such as acetylacetone or nitromethane may be effected[86] (equation 1.11).

$$M(NH_3)_5NCCHCH_2^{\,3+} + {}^-CH_2NO_2 \longrightarrow \{M(NH_3)_5NCCHCH_2CH_2NO\}^{2+}$$
$$\xrightarrow{H^+} M(NH_3)_5(NCCH_2CH_2CH_2NO_2)^{3+} \qquad (1.11)$$

The nitrile function is reduced at room temperature by tungsten hexachloride to give a nitrogen tungsten multiply bonded species (equation 1.12).

$$WCl_6 + ACN \longrightarrow CH_2{=}\,CH - CCl_2 - N \equiv WCl_4 \qquad (1.12)$$

1.5.2 Oligomerization Reactions of Acrylonitrile

This section will be mainly concerned with the dimerization reactions of acrylonitrile. Polymerization reactions of ACN will be ignored as will the preparation of specific trimers and hexamers of ACN since these are usually only encountered as unwanted products in dimerization process. Dimerization of ACN may yield the saturated hydrodimer, adiponitrile (ADN) or the unsaturated dimers, dicyanobutene (DCB), dicyanobutadiene (DCBD) and methylene glutaronitrile (MGN). In addition to coordinatively induced oligomerization, ACN may be oligomerized electrolytically[87-89] or by quenching phosphine initiated anionic polymerization of ACN[90]. The

$NCCH_2CH_2CH_2CH_2CN$

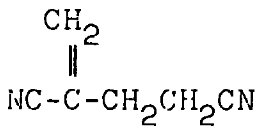
ADN

$NCCH{=}CH_2CH_2CH_2CN$)

$NCCH_2CH{=}CHCH_2CN$) DCB

$NCCH{=}CHCH{=}CHCN$

DCBD

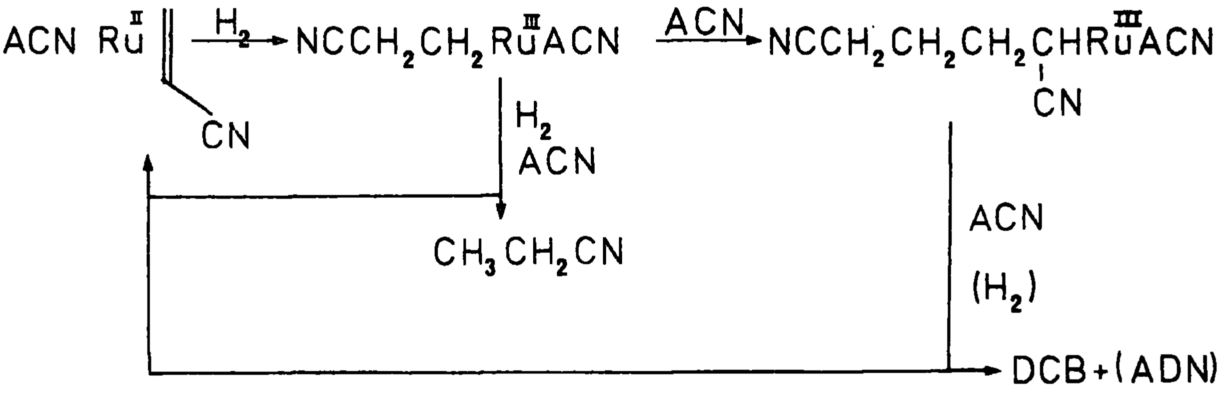


$$\overset{\overset{\displaystyle CH_2}{\|}}{NC\text{-}C}\text{-}CH_2CH_2CN$$

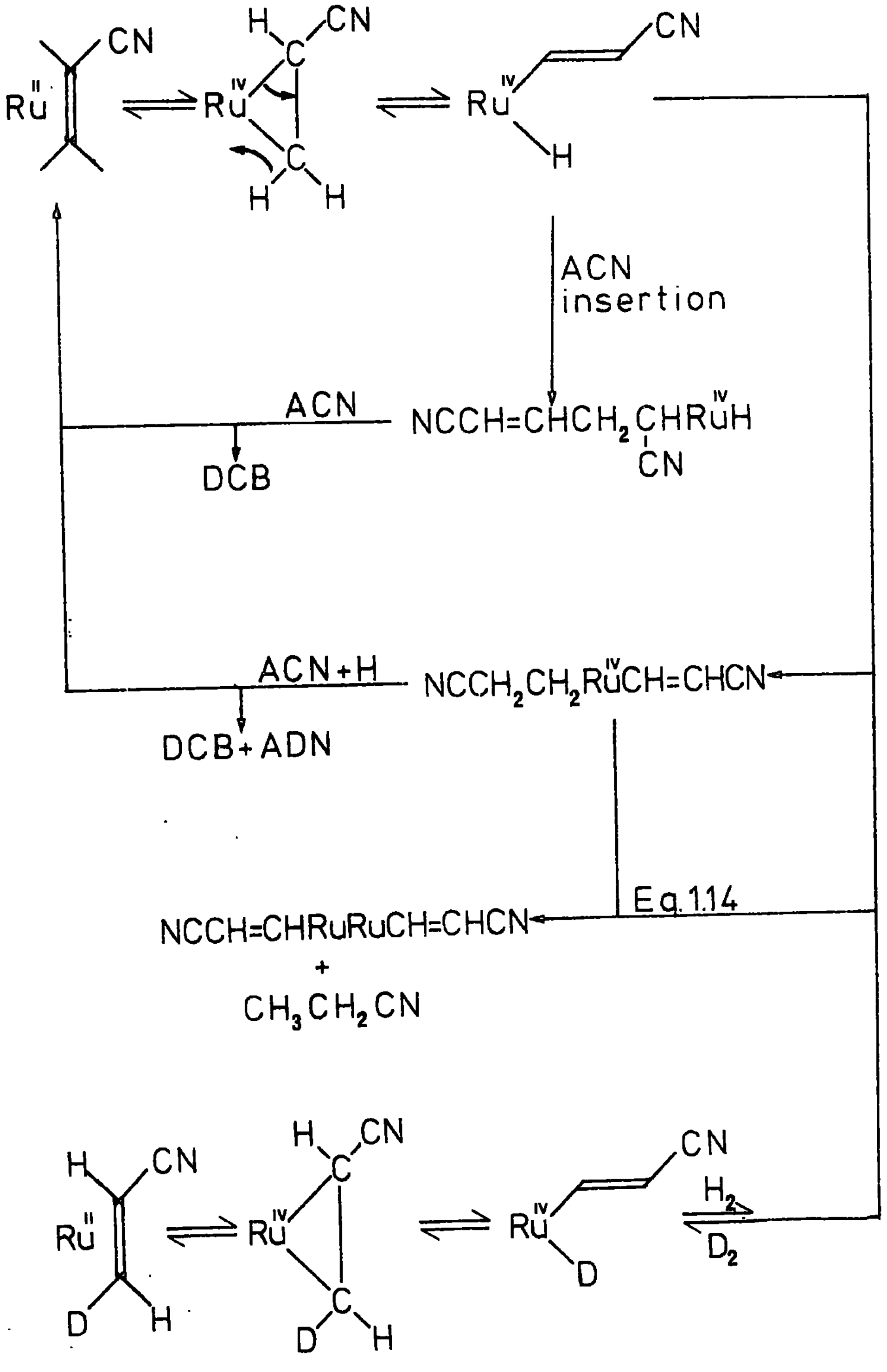
MGN

group of Misono have extensively studied the ruthenium chloride catalysed hydrodimerization of acrylonitrile[62,91-93]. Indeed many ruthenium II and III salts in the presence of hydrogen act as very effective dimerization catalysts[94-100] although the reaction mechanism is still not well established. The reaction of ACN with $RuCl_3.H_2O$ yields $RuCl_2.3ACN$ when conducted under nitrogen but a cyanoethyl complex when under hydrogen[92] and both catalyse the conversion of ACN to propionitrile, ADN and DCB. Tin dichloride or tetraethylammonium trichlorostannate II has been found to reduce the pressure of hydrogen required for dimerization with $RuCl_3.2H_2O$.[101] When hydrogen was replaced by deuterium in the same system, deuterium was found incorporated not only into propionitrile and ADN but also into the *trans* position of the ACN substrate. On this basis the reaction mechanism shown in equation 1.13 (overleaf) is developed. The catalyst generation step is the conversion of the π adduct into a vinyl ruthenium IV hydride. This intermediate may then add or insert a second molecule of ACN and eliminate dicyanobutene. Hydrogenation is effected by a second route involving the formation of a dinuclear ruthenium complex (equation 1.14).

An alternative scheme suggested on the basis of kinetic data[102] favours the formation of a cyanoethyl ruthenium (III) complex followed by insertion of C=C double bond into the carbon ruthenium bond (equation 1.15). The two schemes may not be incompatible since the mechanism may be modified by the addition of a tin species.



Equation 1.15

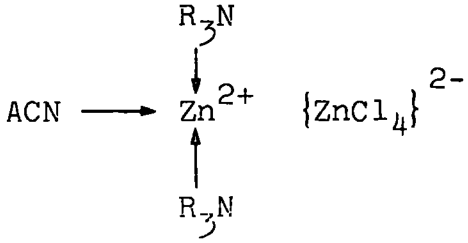


Equations 1.13 and 1.14

Ruthenium and platinum chloro complexes will also catalyse the disproportion of ACN to propionitrile and dicyanobutadiene[130] (equation 1.16).

$$3\ \mathrm{ACN} \xrightarrow{\mathrm{RuCl_3.3H_2O}} \mathrm{CH_3CH_2CN + NCCH = CHCH = CHCN} \qquad (1.16)$$

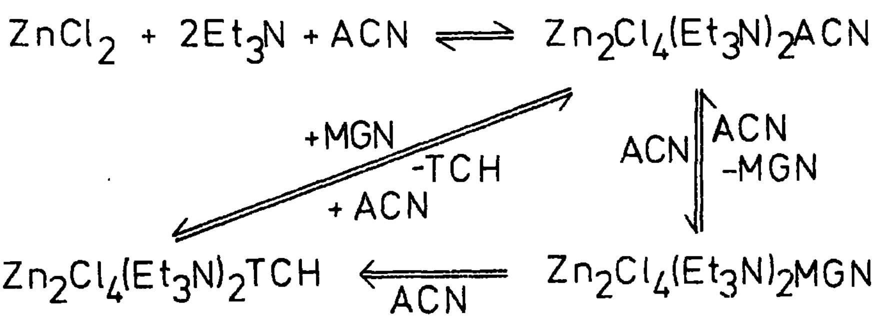
Many metal halides catalyse the oligomerization of ACN to methylene glutaronitrile and 2,4,6 tricyanohexene in the presence of amines or isocyanides. The halides of Ti IV, Cd II, V III, Al III, Fe II, Zn II and Co II (in order of effectiveness) all catalyse the conversion of ACN to MGN in the presence of a trialkyl or aryl amine in yields of up to 75% based on ACN consumed.[103,104] The system will also codimerize ACN with acrylic esters in low yields although neat acrylates were not dimerized. Various patents have extended this reaction to an even wider range of metal salts to include all the first row transition metals with various organic anions.[105-108] The mechanism based on kinetic data from the $ZnCl_2/R_3N$ system requires a 1:2 adduct between ACN and zinc to be the catalytic species, tentatively suggested to have the structure:



$$\mathrm{ACN} \longrightarrow \overset{\overset{R_3N}{\downarrow}}{\underset{\underset{R_3N}{\uparrow}}{Zn^{2+}}} \quad \{ZnCl_4\}^{2-}$$

The reaction scheme proposed is shown in equation 1.17. If the amine is replaced by an alkyl isocyanide, acrylatesand ACN are dimerized to branch chain oligomers and polymers.[109,110]

A number of nucleophilic anionic metal complexes also catalyse the dimerization of ACN. N,N´ ethylenebis(salicylideneiminato)



Equation 1.17

cobalt I, (Co salen), (Figure 1.14) catalyses the oligomerization of ACN to MGN, equation 1.18, in the presence of a quenching agent such as *tert* butanol.[111] The intermediate

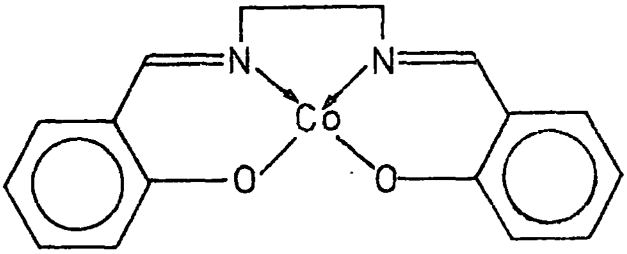
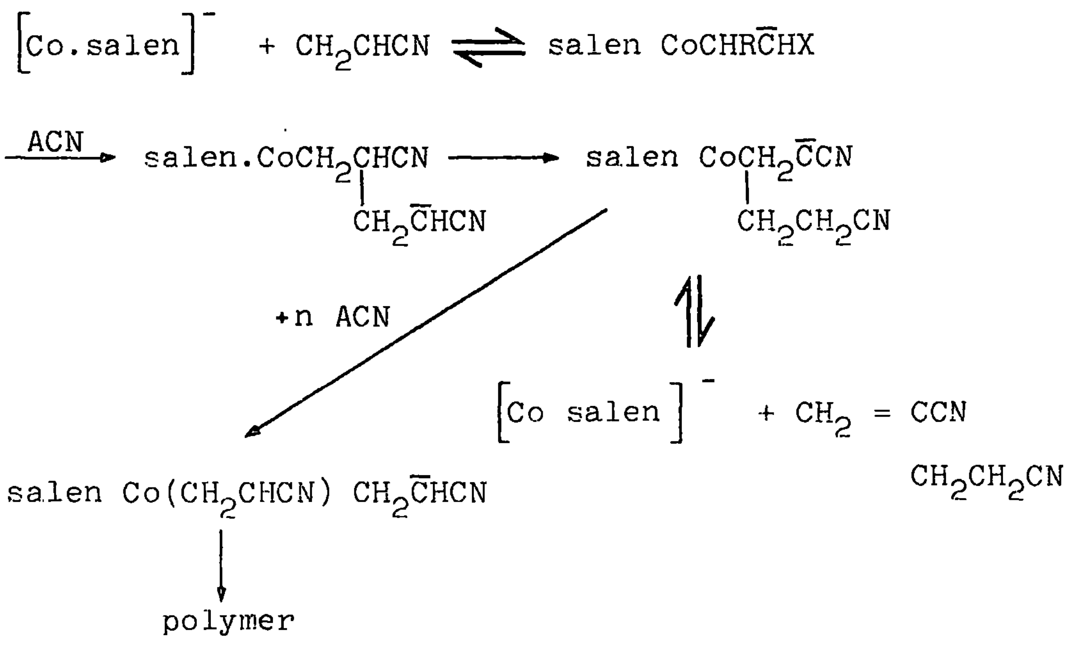


Figure 1.14

salen Co $CH_2\bar{C}HCN$, is closely related to the intermediate in the tertiary phosphine catalysed oligomerization, $R_3\overset{+}{P}CH_2\bar{C}HCN$ [87,90] as are the products

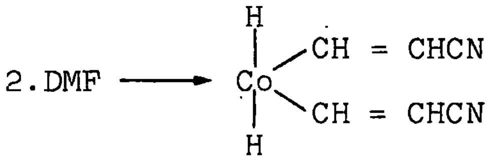


(1.18)

Other nucleophiles which dimerize ACN include $HFe(CO)_4^-$, $HFe_2(CO)_8$. $HFe_3(CO)_{11}$ and $Fe(CO)_5$ or $Co_2(CO)_8$ reduced by $NaBH_4$ or $LiAlH_4$.[112] Whilst these yield ADN, MGN and propionitrile it seems highly likely that the mechanism is nucleophilic. Non-catalytic dimerization has been achieved by reacting a metal halide and a strongly reducing metal in a polar solvent[113-119], e.g. equation 1.19. The yield is

$$\text{ACN} + \text{CoCl}_2 + \text{Mn} \xrightarrow{\text{DMF}} ? \xrightarrow{H_2O} \text{ADN} \qquad (1.19)$$

stoichiometric on reducing metal consumed. The intermediate was suggested to have the structure:[119]



The hydrolysis step may be replaced by pressurizing with hydrogen[113,116] (see discussion in Chapter Six).

1.5.3 Acrylonitrile Complexes as Catalysts

The catalytic activity of bis(ACN)nickel has been reviewed by Schrauzer[13] and more recently its effectiveness as a cycloaddition catalyst has been employed in the reaction of bicyclo(1,1,0) butanes with olefins[120-125]. The zinc chloride, acrylonitrile complex has also been used as a cycloaddition catalyst[126] as well as a polymerization or copolymerization catalyst although this is outside the scope of this review.[127-129]

CHAPTER TWO

Some N bonded Acrylonitrile and Related Nitrile complexes of some Metal Chlorides

2.1 Introduction

The complexes between nitriles and metal salts have been extensively investigated and the subject of a number of reviews.[1-3] Nitriles are particularly useful solvents for metal chlorides and therefore many studies have concentrated on the solution behaviour of metal halides in nitriles. Acetonitrile has been examined as a solvent very extensively. The solvates fall into two categories. The first are the non-ionic adducts such as $SnCl_4$.2MeCN[4], BX_3.MeCN[5] and many others of general formulation MCl_n.mMeCN where M=Mg,Ni,Cd, Ga,In and Tl, etc.[6,7]

The second type are the ionic adducts where the nitrile is bound to a cationic centre. Ionic solids have been isolated by the technique of mixing a metal chloride with a powerful halide abstractor such as $SbCl_5$, $SnCl_4$ or BCl_3. By this method adducts of the general formation $ML_n{}^{p+}$ $(M'Cl_4{}^{q-})_{p/q}$ where M is a main group or transition metal, M = B, Al, Ga, In, Tl, Fe, Sb and L = MeCn, Bu^tCN, PhCN.[8-12] The ionic nature of the adducts in solution has been confirmed by conductance[11] and potentiometric[12] measurements. However more frequently the nature of the adducts has been deduced from the method of synthesis and occasionally ligand field spectra.[8-10]

Acrylonitrile shows similar N bonded coordination chemistry to the aliphatic nitriles, forming adducts which are probably non-ionic in the crystalline state such as $ZnCl_2$.2ACN[13,14], $TiCl_3$.3ACN[13], $TiCl_4$.2ACN[13,15,16] and MCl_5.ACN[17-21] (M = Nb, Ta, Sb) and also ionic adducts such as $Cu(ACN)_4ClO_4$[22], $M(ACN)_6{}^{2+}$ $(SbCl_6{}^-)_2$[23] and $M(ACN)_6$ $(InCl_4{}^-)_2$.[23]

In the coordination chemistry of both acrylonitrile and aliphatic nitriles however there are systems which cannot be categorized because of a lack of or conflicting data. For example considerable attention has been devoted to the $AlCl_3$-nitrile systems. On the basis of ^{27}Al NMR the equilibrium in equation 2.1 has been proposed to exist in solution.[24]

$$4AlCl_3 + 6RCN \rightleftharpoons Al(RCN_6)^{3+} + 3AlCl_4{}^{2-} \qquad (2.1)$$

Vibrational spectra of solutions and of the solid adduct $AlCl_3.2MeCN$ confirm the presence of the $AlCl_4{}^-$ anion.[25] Very recently Beattie and coworkers[26] have attempted to resolve the nature of the cationic species in the system. From conductimetric data on mixtures of Et_4NCl or LiCl with $AlCl_3$ in MeCN they conclude that equation 2.1 or 2.2 or a linked equilibrium of the two is most favourable.

$$3AlCl_3 + 5MeCN \rightleftharpoons \left[AlCl(MeCN)_5\right]^{2+} + 2AlCl_4{}^- \qquad (2.2)$$

They also found the formulation in equation 2.2 to exist in the solid adduct $AlCl_3.2MeCN$ which was shown by an X-ray structure determination to exist as $\left[AlCl(MeCN)_5\right]^{2+}\left[AlCl_4{}^-\right]_2.MeCN$.

This system has been outlined in some detail since it illustrates the problems encountered in attempting to deduce the structure of the solid adduct and its solution. Similar solution equilibria are believed to occur in the systems $CrCl_3$ + ACN[27] and $CoCl_2$ + MeCN.[28] In view of the uncertainty regarding the structure of many of the acrylonitrile adducts and the importance of the metal chlorides as Ziegler Natta catalysts in acrylonitrile polymerization,[29] initiators in (co)polymerization,[30-32] and cyanoethylations reactions[34-37] we have studied some of the systems and compounds placing emphasis on those compounds whose formulation appears inconsistent with their likely structure. We used the work of Kern[13] as an entry point since this represents the earliest significant study of acrylonitrile with the first row transition metals.

In this chapter we will characterize a new cationic complex of acrylonitrile, $Ni(ACN)_6^{2+}$, which crystallizes with the rare anion $Zn_2Cl_6^{2-}$ and will demonstrate that propionitrile also forms a similar complex. The synthesis of a range of adducts and the reaction of iron trichloride and nickel chloride with acrylonitrile is also discussed.

2.2 Experimental

$CoCl_2$ and $NiCl_2$ were prepared from hydrated commercial samples (BDH) by refluxing for 24 hrs. with thionyl chloride.

Zinc chloride was prepared by dissolving Zn metal in diethyl ether saturated with hydrogen chloride. The solution of $ZnCl_2$ was filtered to remove unreacted Zn metal and the ether pumped off. This was found to give $ZnCl_2$ of at least 99.5% purity. $FeCl_3$ was purified by vacuum sublimation of commercial anhydrous samples (BDH) and $TiCl_4$ and $SnCl_4$ by vacuum distillation. Analytical data and infra-red spectra for all compounds are listed in Tables 2.1 and 2.2 respectively.

$MCl_4.2ACN$ (M=Ti,Sn): 5 ml. of MCl_4 was added to 30 ml. of ACN in a cooled flask. Any immediate precipitate was redissolved by warming the solution. On standing or reduction of volume the solution yielded white (M=Sn) or yellow (M=Ti) volatile crystals which were collected on a filter and washed with cold ACN.

$CoCl_2$.ACN: 5g. of dry $CoCl_2$ was refluxed in 25 ml. of dry ACN for 1 hr. Excess undissolved $CoCl_2$ was filtered from the blue solution and on standing the liquors yielded a microcrystalline purple solid which was separated on a glass frit and washed with cold ACN. The adduct was dried in a stream of dry N_2 which changed the purple solid to a blue solid. (The purple solid could not be isolated, dry, from the liquors).

$ZnCl_2$.2ACN: 5g. of anhydrous $ZnCl_2$ was dissolved in 30 ml. of ACN. The reaction was very exothermic and cooling the solution yielded colourless needles. These were collected on a sinter and dried in dry N_2. They were soft, low melting and very air sensitive so that difficulty was encountered in obtaining good analyses or infra-red spectra.

Fe_2Cl_3.6ACN: 5g. of anhydrous $FeCl_3$ was added to 20 ml. of acrylonitrile and the mixture warmed until complete dissolution had occurred giving a yellow green solution. A slight insoluble residue was filtered off and the solution cooled to give brown-green crystals. They were collected on a sinter and dried in a stream of N_2.

$Ni(MeCN)_6{}^{2+}ZnCl_4{}^{2-}$: The adduct was prepared by 2 methods:

(1) 1.1g. of $NiCl_2$, 2g. of Zn dust and 1g. of dry sand (to prevent caking) were placed in a Soxhlet thimble and extracted with 70 ml. of acetonitrile for 18 hrs., when the liquors had turned royal blue. On cooling the solution afforded purple crystals which were separated and dried in a stream of nitrogen to give *hexakis* acetonitrile nickel II tetrachlorozincate.

(2) 4.4g. of $NiCl_2$ and 6.7g. of $ZnCl_2$ were ground together in a glove box and refluxed with 50 ml. of dry acetonitrile for 6 hrs. after which the yellow slurry had turned the liquors blue. Excess $NiCl_2$ was filtered from the hot liquid and on cooling purple crystals of *hexakis* acetonitrile nickel II tetrachlorozincate were formed.

$Ni(ACN)_6{}^{2+}Zn_2Cl_6{}^{2-}$: Prepared by 2 methods:

(1) 3g. of *hexakis* acetonitrile nickel II tetrachlorozincate were dissolved in 10 ml. of acrylonitrile. The liquors from the blue solution were pumped off and the procedure repeated twice more. The final liquors were allowed to stand at 0°C for several days whereupon they yielded purple crystals of *hexakis* acrylonitrile nickel II hexachlorodizincate.

(2) $NiCl_2$(4.6g) and $ZnCl_2$(10g) were refluxed together in 30 ml. of ACN for 5 hrs. after which time the solution was deep blue. Unreacted $NiCl_2$ was filtered from the hot liquors and on cooling purple crystals of *hexakis*acrylonitrile nickel II hexachlorodizincate were formed.

$Ni(EtCN)_6{}^{2+}Zn_2Cl_6{}^{2-}$: This was prepared by the same method 1 as for $Ni(ACN)_6{}^{2+}Zn_2Cl_6{}^{2-}$.

The reaction of $NiCl_2$ + ACN: 5g. of $NiCl_2$ were placed in a soxchlet thimble and extracted with 50 ml. of dry ACN for 4 hrs. After 1 hr. the solution had turned dark yellow and yielded a dark yellow precipitate insoluble in excess ACN. Consistent analyses could not be obtained for this yellow solid although the analyses approximated to $NiCl_2.ACN_{1.5}$ and it was not investigated further.

$NiSb_2Cl_6.6ACN$: 5g. of $NiCl_2$ was refluxed as a slurry with 11.6g. of $SbCl_5$ dissolved in 50 ml. of ACN for 26 hrs.; the solution had turned brown. A further 50 ml. of ACN was added

TABLE 2.1 Analyses for Nitrile-Metal Chloride Adducts*

Compound	C	H	N	Cl	Other
$CoCl_2$.ACN	20.2(19.7)	1.6(1.6)	8.0(7.7)	37.8(38.8)	Co:32.0(32.2)
$ZnCl_2$.2ACN	28.3(29.7)	2.9(2.5)	11.0(11.5)	29.1(29.2)	Zn:28.0(26.9)
$TiCl_4$.2ACN	24.5(24.3)	2.4(2.0)	9.6(9.6)	47.8(48.0)	Ti:14.1(16.2)
$SnCl_4$.2ACN	19.9(19.6)	1.2(1.6)	7.5(7.6)	39.1(38.6)	
$NiZn_2Cl_6$6ACN	30.3(30.0)	2.0(2.5)	11.6(11.6)	30.4(29.6)	Ni:7.9(8.1) Zn:17.8(18.1)
$NiZnCl_4$.6MeCN	26.0(28.1)	4.2(3.5)	15.1(16.4)	27.9(27.7)	Ni:11.6(11.5) Zn:13.0(12.8)
$NiZn_2Cl_6$.6EtCN	29.2(29.5)	4.6(4.1)	11.3(11.5)	25.7(29.1)	Ni:7.6(8.0) Zn:17.8(17.9)
Fe_2Cl_8.6ACN	30.0(30.3)	2.9(2.5)	10.4(11.8)	40.1(39.8)	Fe:16.1(15.7)

* Required in Parentheses

since the solution was solid. On cooling the diluted solution, apparently brown needlelike crystals were formed which on separation and washing turned to a pale grey in colour. Analysis showed them to be *hexakis* acrylonitrile nickel II bis hexachloroantimonate.

2.3 Results and Discussion

2.3.1 The Solid Adducts

The adducts all show an increase in the C≡N stretching frequency with no change in the C=C stretch (Table 2.2) as expected for an N bonded acrylonitrile adduct (see discussion in Chapter One). The adducts $TiCl_4.2ACN$ and $SnCl_4.2ACN$ are both volatile crystalline solids having a vapour pressure of about 5 mm.Hg. at room temperature. Far infra-red studies[20] and dipole moment measurements[15] indicate a *cis* stereochemistry which is confirmed in $SnCl_4.2ACN$ by ^{35}Cl nuclear quadrupole resonance spectroscopy in Chapter Five. The structure of *bis*-acrylontrile zinc dichloride is not known. However the acetonitrile analogue, whose crystal structure has been determined[38], contains tetrahedral coordinate zinc with only weak Van der Waals interactions between adduct molecules. The ACN adduct probably has a similar structure with greater distance between adduct molecules due to the greater size of the ligand. This would account for its unusually low melting point (38°C). The structure of the monoacrylonitrile cobalt chloride adduct is unclear and in the absence of further information such as reflectance uv/visible spectra or other established nitrile analogues no deductions regarding the structure may be made.

TABLE 2.2 Infra-Red Spectra of Nitrile-metal halide Adducts 4000-400 cm^{-1}

Compound	Absorption Maxima/cm^{-1}
ACN (free)	2228^*, $1605^\dagger$
$CoCl_2$·ACN(n)	3065m, 3030m, $2290w^*$, $2265s^*$. $1606m^\dagger$, 1405s, 1285w, 1090w, 975m, 964s, 723w, 675w
$ZnCl_2$·2ACN(f)	3110m, 3070m, $2305sh^*$, $2290s^*$, $1610m^\dagger$, 1415m, 970sh, 968s, 900m, 685m
$TiCl_4$·2ACN(n)	3110w, 3050w, $2300w^*$, $2265s^*$, $1600w^\dagger$, 1400m, 985m, 978m, 955m, 835w, 775w, 678w, 580w
Fe_2Cl_8·6ACN(n)	3110w, 3070w, $2305sh^*$, $2290s^*$, $1610m^\dagger$, 1415m, 970sh, 968s, 900m, 685m
$Ni(SbCl_6)_2$6ACN(n)	3120w, 3070m, $2305w^*$, $2280s^*$, $1610m^\dagger$, 1418m, 985m, 965m, 730w, 688w
$NiZn_2Cl_6$·6ACN(n)	3120w, 3080w, $2300w^*$, $2280s^*$, $1610s^\dagger$, 1415m, 1090, 1060w, 1020w, 994m, 985m, 962w, 890w, 723w, 672m
$NiZnCl_4$·6MeCN(n)	2310s, $2296s^*$, 1035m, 940w, 722w
$NiZn_2Cl_6$·6EtCN(n)	$2305s^*$, 1418m, 1315w, 1020m, 790m, 730w, 578w
$NiCl_2$·1.5ACN(n)	3120w, 3075w, $2210m^*$, 1405m, 1092w, 985m, 965m, 735w, 672w

f = Fused
n = Nujol Mull
$*$ = $\nu(C{\equiv}N)$
$\dagger$ = $\nu(C{=}C)$

2.3.2 Adducts Containing Nickel Chloride

There have been a number of studies of nickel halide-nitrile systems and several of the adducts have been extensively characterized. However the situation is confused by the claimed preparation of a number of complexes of doubtful formulation.

Russian workers have isolated the "sky blue" adduct $NiCl_2.2MeCN$[47], from sealed tube reactions, whilst other workers have reported the same formula compound as yellow green.[41] Complexes of the formulation $NiCl_2.4MeCN$[47] and $NiCl_2.MeCN$[6] have also been claimed. In contrast Kem[13] and Beech[48] found that MeCN and EtCN did not react with anhydrous nickel chloride at normal pressures. The situation was further complicated by the claimed isolation of the adducts $NiCl_2.2EtCN$, $NiCl_2.3.5MeCN$ and $NiCl_2.3ACN$ from nickel chloride, zinc metal admixtures. Recently the acetonitrile nickel chloride system has been studied by differential scanning calorimetry and thermal gravimetry,[49] the results conclusively demonstrating the existence of $NiCl_2.2MeCN$ and, on heating, its decomposition by loss of ligand to $NiCl_2.MeCN$. Lower ratios of MeCN to $NiCl_2$ were also observed, e.g. $NiCl_2(MeCN)_{0.88}$.

We have re-examined the reactions and products of reference 13. The yellow powder from the reaction of $NiCl_2$ with ACN is similar to that obtained by Kem in physical and spectral appearance. Its insolubility in ACN strongly suggests a polymeric structure, an interpretation further strengthened by the absence of a C=C double bond absorption in the infra-red spectrum indicating that free ACN is no longer present. The variable analytical data would indicate that the nickel chloride is not stoichiometrically bound to the polymer but loosely trapped or intercalated in a polymeric matrix.

We have found the nickel chloride, zinc, nitrile systems to yield $NiL_6^{2+}ZnCl_4^{2-}$, L=MeCN and $NiL_6^{2+}Zn_2Cl_6^{2-}$ L=EtCN, ACN. The acetonitrile adduct was believed to be $NiCl_2.3MeCN$[13] until a crystal structure showed it to contain the tetrachlorozincate ion.[43] We independently demonstrated that the role of the zinc metal was not simply reductive as claimed[13] but was also incorporated into the final structure, as zinc chloride. Reduction of nickel chloride by zinc yields zinc chloride. Since zinc chloride is a moderately good chloride acceptor it aids the dissolution of nickel chloride as the solvated NiL_6^{2+} cation. Acrylonitrile and propionitrile also undergo similar solvation reactions to give *hexakis*-nitrile nickel II salts but the structures contain the rare hexachlorodizincate anion.

2.3.3 The Crystal Structure of $Ni(ACN)_6^{2+}Zn_2Cl_6^{2-}$

The crystal structure of this adduct was determined by Dr. Stephen Wallwork of the University of Nottingham by standard X-ray techniques. The molecular units are shown in Figure 2.1 with selected internuclear distances and angles given in Tables 2.3 and 2.4. The unit cell is illustrated in Figures 2.2.a,b. The cation shows the expected octahedral symmetry with slight distortion perhaps due to crystal packing. The average C≡N distance is 3 pm. shorter than in free acrylonitrile[39] although this is within the e.s.d. of the data. A shortening of 22 pm. has been found in accurate studies of $BF_3.MeCN$ adduct.[5] The hexachlorodizincate anion is binuclear with tetrahedral coordinate zinc and bridging chlorine atoms.

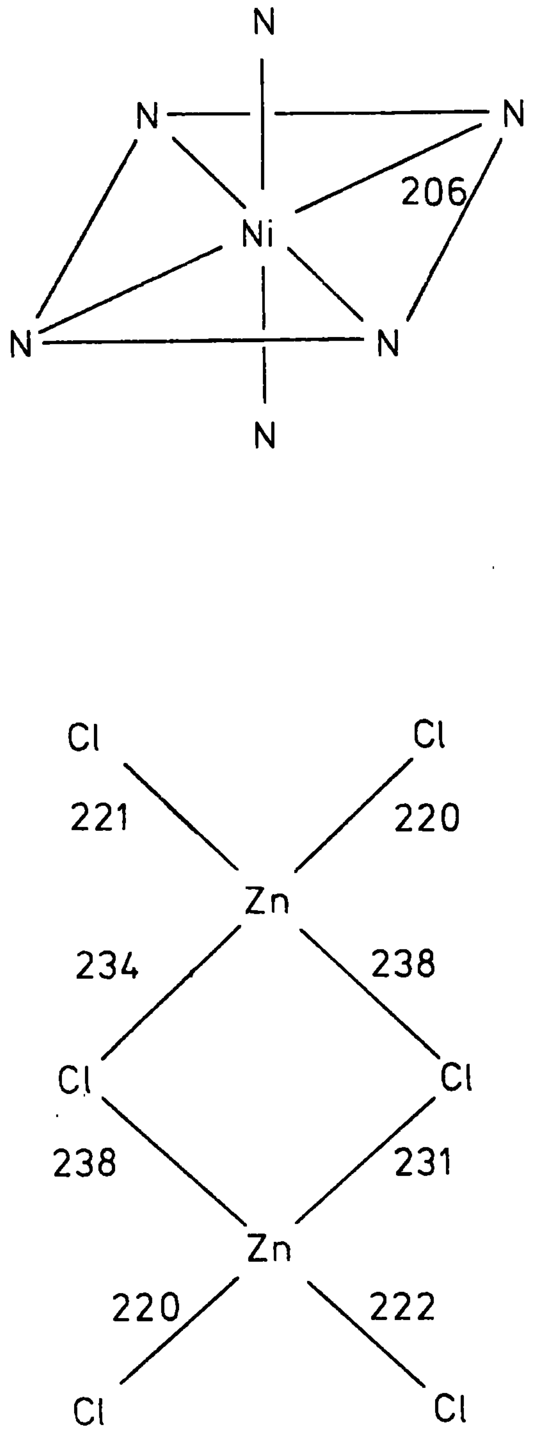

N
N
N
206
Ni
N
N
N
Cl
Cl
221
220
Zn
234
238
Cl
Cl
238
231
Zn
220
222
Cl
Cl

Figure 2.1

TABLE 2.3 Selected Bond Lengths for $Ni(ACN)_6Zn_2Cl_6$ *

$Ni-N_1$	203(1)	av = 205(5)				
$Ni-N_2$	204(4)					
$Ni-N_3$	206(5)					
$Ni-N_4$	206(5)					
$Ni-N_5$	207(5)					
$Ni-N_6$	205(4)					
N_1-C_1	112(5)	av=113(5)	C_1C_2	148(7)	C_2C_3	125(7)
N_2-C_4	114(5)		C_4C_5	171(12)	C_5C_6	143(1)
N_3-C_7	108(6)		C_7C_8	162(8)	C_8C_9	127(6)
N_4-C_{10}	113(6)		$C_{10}C_{11}$	151(8)	$C_{11}C_{12}$	124(8)
N_5-C_{13}	111(5)		$C_{13}C_{14}$	150(7)	$C_{14}C_{15}$	123(7)
N_6-C_{16}	120(5)		$C_{16}C_{17}$	148(8)	$C_{17}C_{18}$	125(10)
Zn_1Cl_1	219(2)		Zn_1Cl_3	239(2)		
Zn_1Cl_2	222(2)		Zn_1Cl_4	229(1)		
Zn_2Cl_5	221(2)		Zn_2Cl_3	232(1)		
Zn_2Cl_6	220(2)		Zn_2Cl_4	240(2)		

TABLE 2.4 Selected Bond angles for $Ni(ACN)_6Zn_2Cl_6$ *

N-Ni-N (av)	90(2)		
$Cl_1Zn_1Cl_2$	116(1)	$Cl_3Zn_2Cl_4$	92
$Cl_1Zn_1Cl_3$	111(1)	$Cl_5Zn_2Cl_3$	110(1)
$Cl_2Zn_1Cl_4$	118(1)	$Cl_4Zn_2Cl_6$	107(1)
$Cl_3Zn_1Cl_4$	93(1)	$Cl_5Zn_2Cl_6$	118(1)

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* Refinement incomplete, preliminary data only

Figure 2.2.b View of Unit Cell of $Ni(ACN)_6^{2+}Zn_2Cl_6^{2-}$ on B Axis

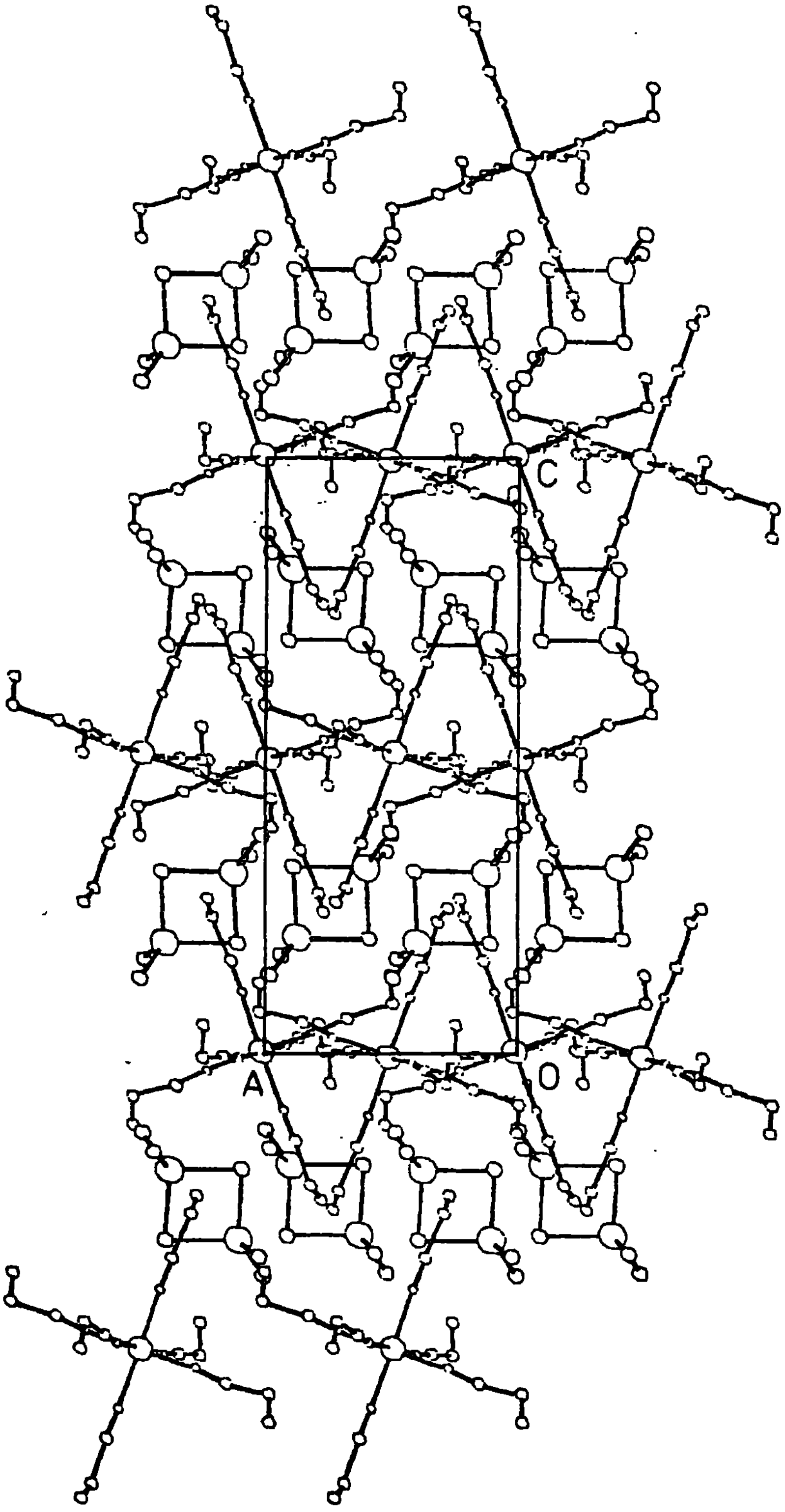
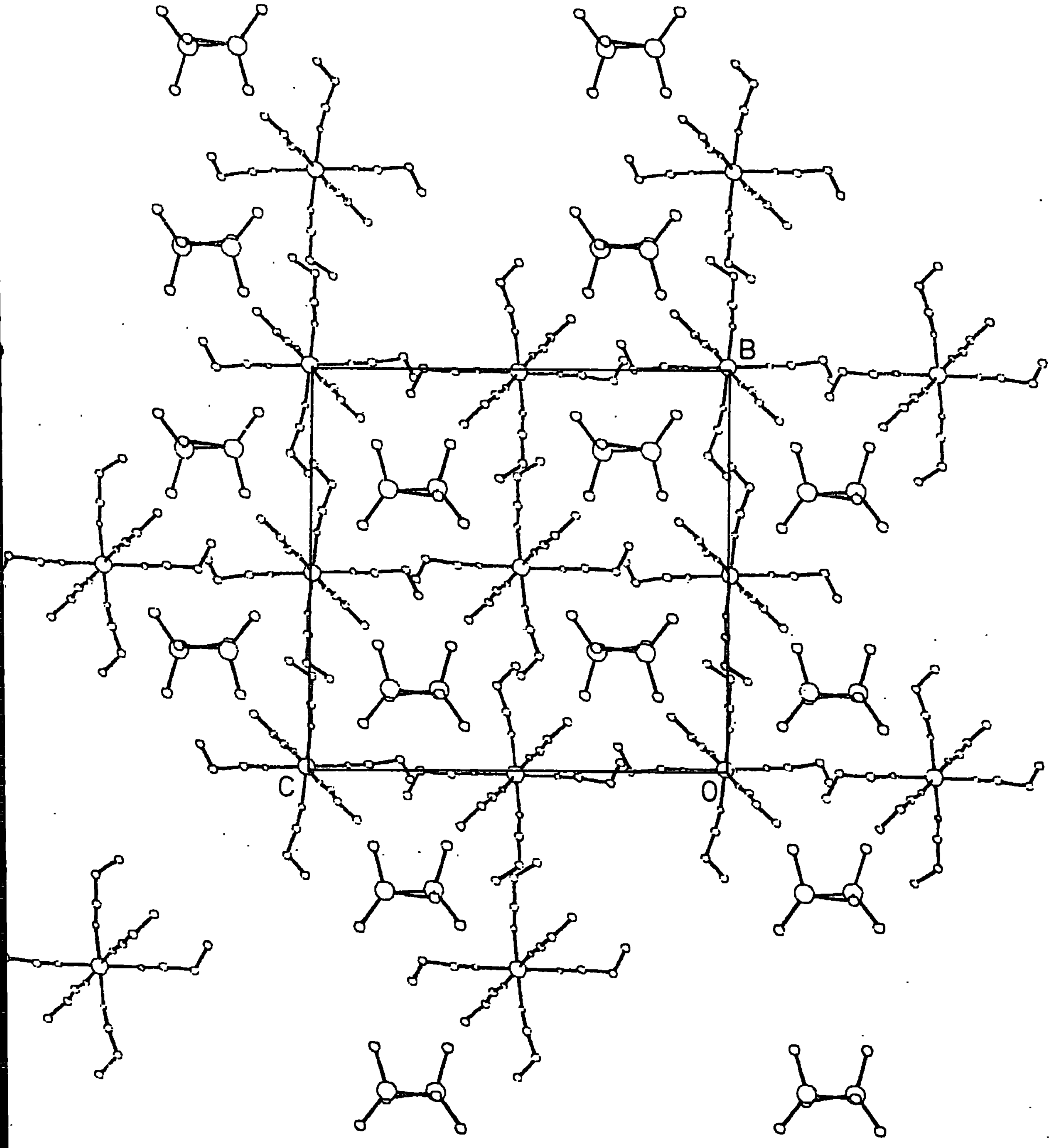


Figure 2.2.a View of Unit Cell of $Ni(ACN)_6^{2+}Zn_2Cl_6^{2-}$ on A Axis



The $Zn_2Cl_6{}^{2-}$ dimer has been characterized previously in $(Cp_2TiDME_2)\overset{*}{Zn_2}Cl_6.Bz$[40] and $\left[(\pi C_6H_{11})Ni(PPh_3)_2{}^{+}\right]_2Zn_2Cl_6{}^{2-}$ [41] although full structural data was not published for the latter compound.

The chlorine bridges in our compound are slightly assymmetric with an 8-10 pm. difference in bond length compared with 14 pm. difference in reference 40. The terminal Zn-Cl distances, 2.21 pm. are significantly shorter than the bridging Zn-Cl distances of 230 pm. and 240 pm., as expected, similar to the Al_2Cl_6 dimer.

In contrast the analogous acetonitrile compound, hexakisacetonitrile nickel tetrachlorozincate, has been shown to contain a monomeric anion[43]. The reason for this is probably a crystal packing effect of the cation size. It is noteworthy that the hexachlorodizincate anion is associated with large cations in the other two structures known to contain this anion.[40,41]

2.3.4 The Reaction of Iron Trichloride with Acrylonitrile

We were unable to prepare the simple $FeCl_3$ adduct with acrylonitrile. The analyses indicate that one third of the iron is present as Fe^{II}. The reduction of Fe^{III} must proceed with a simultaneous oxidation (in the form of chloronation) of acrylonitrile although no attempt was made to isolate any organic products. The reduction of $FeCl_3$ by nitriles has been shown to be catalysed by small amounts of water[44]. When the solvents are perfectly dry the adducts $FeCl_3.nRCN$ $(1.7<n<3)$ $(R=Me,Ph,CH_2Cl,Et)$ may be isolated and a preliminary crystal structure[44] of the propionitrile adduct indicates that each unit cell consists of $8FeCl_4{}^-$ units and $4Fe(EtCN)_5Cl^{2+}$

x DME dimethoxy ethane

cations.[44,45] Acetonitrile reacts analogously with acrylonitrile, and the adduct has been formulated as $Fe^{2+}(MeCN)_6(FeCl_4^-)_2$ on the basis of ligand field and Moessbauer spectra. We consider the acrylonitrile adduct to have a similar formulation. The partial reduction of iron III may be explained by the increase in the reduction potential of iron III by coordination of the chloride ion. If a good chloride acceptor such as $SbCl_5$ or $SnCl_4$ is added to the reaction, the reduction has been found to proceed to completion whereas the reduction is totally inhibited if a chloride donor (e.g. LiCl, $NiCl_2$) is present, where the tetrachloroferrate III salt is formed (equations 2.3, 2.4).

$$FeCl_3 + 2SbCl_5 \xrightarrow{\text{XS MeCN}} Fe^{II}(MeCN)_6 + 2SbCl_6 + ? \qquad (2.3)$$

$$LiCl + FeCl_3 \xrightarrow{\text{XS MeCN}} Li(MeCN)_6^+ + Fe^{III}Cl_4^- \qquad (2.4)$$

If $FeCl_3$ is ionized in nitriles as $Fe(RCN)_mCl_n^{3-n+}$ and $FeCl_4^-$ only the cationic part of the iron will undergo reduction to iron II (equation 2.5).

$$Fe\ (RCN)_mCl_n^{3-n-} + FeCl_4^- \xrightarrow[\text{Trace}\ H_2O]{\text{ACN}} Fe(RCN)_6^{2+} + FeCl_4^- \qquad (2.5)$$

2.3.5 The Solution Behaviour of metal Chloride Acrylonitrile Adducts

The behaviour of a metal halide in a solvent such as a nitrile is governed by a number of factors, the most important probably being dielectric constant, Lewis acidity of the solute and basicity of the solvent and the maximum coordination number of the metal.

The determination of solution behaviour is both difficult and laborious due to the variety of techniques such as ligand field spectroscopy, conductivity, multinuclear NMR, etc. needed to gain an accurate model of the solution. For this reason no attempt has been made to measure any solution parameters of the acrylonitrile adducts and this discussion will be restricted to what can reasonably be inferred from the wealth of information on acetonitrile solvent systems. Comparison of the degree of ionization of a number of metal chloride complexes in a single solvent enables factors such as dielectric constant to be ignored. The ionization is then dependent on the strength of the metal-chlorine bond and the donor capacity of the nitrile (namely the relative donor capacity of a chloride ion *vs* the nitrile).

Hence the $ZnCl_2$,MeCN system undergoes partial solvolysis[50] according to equation 2.6.

$$3ZnCl_2.2L + 2L \rightleftharpoons Zn(MeCN)_6^{2+} + 2(ZnCl_3L^-) \qquad (2.6)$$

In the cobalt dichloride-acetonitrile system a more complete two part solvolysis has been established by conductivity measurements and ligand field spectra[51], equation 2.7.

$$\begin{aligned} &CoCl_2.4MeCN(s) \xrightleftharpoons{\text{XS MeCN}} CoCl_2.2MeCN + 2MeCN \quad k = 312 \\ &2CoCl_2.2MeCN + 2MeCN \rightleftharpoons Co(MeCN)_6^{2+} + CoCl_4^{2-} \quad k = 0.38 \end{aligned} \qquad (2.7)$$

Due to the poor solubility of nickel chloride in nitriles no comparable study has been made of the $NiCl_2$-MeCN system although formation of the complex anions $(NiCl_3L)^-$ has been observed by Libus in this system[52] indicating some kind of coordinative dissociation. Finally no studies have revealed any ionization in the $TiCl_4$.2RCN or $SnCl_4$.2RCN systems. The reason for this is that the metals are already coordinatively saturated unlike previous examples and therefore any dissociation will involve the rupture of a metal-chlorine bond with the formation of a weaker dative metal nitrogen bond. The very high strength of the TiCl bond (494 kJ mol^{-1})[53] and Sn-Cl bond (414 kJ mol^{-1})[53] compared with Zn-Cl (230 kJ mol^{-1})[54] precludes any such dissociation. Metal chloride acrylonitrile systems would be expected to show broadly similar behaviour to the acetonitrile systems discussed above since the donor capacity, dielectric constant and solid state coordination behaviour are very similar. However precise discussion is unjustified in view of the dearth of information.

2.4 Summary

Metal chloride adducts have been prepared by a variety of routes. Whilst some adducts, e.g. $TiCl_4.2RCN$, $SnCl_4.2RCN$ are essentially non-ionic in nature others with weaker M-Cl bonds and better halide acceptor power such as in the $NiCl_2$/$ZnCl_2$/RCN system are ionic. A simplified synthesis of $Ni(MeCN)_6ZnCl_4$ from $NiCl_2$ and $ZnCl_2$ has been demonstrated and the new compound $Ni(ACN)_6Zn_2Cl_6$ has been prepared and its structure verified by X-ray analysis by outside workers.

In between the two extremes of coordinative dissociation, the adducts $CoCl_2.ACN$ and $ZnCl_2.2ACN$ are considered to be neutral in the solid whilst solvolysis in acrylonitrile giving an ionized solution is indicated from by comparison with the corresponding acetonitrile data.

Finally the reaction of $FeCl_3$ with nitriles giving $Fe^{II}L_6{}^{2+}$ $Fe^{III}Cl_4{}^-$ has been rationalised on the basis of modification of the electrode potential of Fe^{III} by coordination with chloride ion.

CHAPTER THREE

The Relative Lewis Acidities of Silicon Germanium and Tin Tetrachlorides towards some Lewis Bases: A Vapour Pressure, Composition Study

3.1 Introduction

The Lewis Acidities of the Group IV halides have been extensively studied[1-12] and their Lewis Acidities are known to increase in the sequence $CCl_4 < SiCl_4 < GeCl_4 << SnCl_4 > PbCl_4$.[13] Whereas no interaction of carbon tetrahalides with Lewis bases is normally observed the other tetrahalides show the ability to coordinate to strong Lewis bases to give mono- and bis-adducts, equation 3.1

$$MX_4 + L \rightleftharpoons MX_4.L \overset{L}{\rightleftharpoons} MX_4.2L \qquad 3.1$$

Tin IV chloride forms the widest range of stable adducts, $SnCl_4.2L$[1-4], soluble in inert solvents with varying degrees of dissociation[5-8].

Fewer silicon[2,3,9] and germanium[2,3] analogues $SnCl_4.2L$ and $GeCl_4.2L$ have been isolated and characterised.

Cryoscopic studies[10,11] suggest that $SiCl_4$ and $GeCl_4$ exhibit only a slight interaction with ethers whilst $SnCl_4$ forms compounds with a wide range of aromatic and aliphatic ethers and where isolable adducts of all three tetrachlorides are formed with the evolution of less heat than the tin adducts. Thermometric titration[14,15] demonstrates the ease of formation of the adducts and other calorimetric studies[16,17] of the reaction of pyridine or isoquinoline between $SiCl_4$, $GeCl_4$ and $SnCl_4$ show that the heats of formation of the adducts increases in that sequence.

Adducts between germanium tetrachloride or silicon tetrachloride and nitriles or ethers[3,19] have never been isolated. Nevertheless a feebly bonding interaction between $SiCl_4$ or $GeCl_4$ and weak donors such as ethers and nitriles would be expected which would then cause the mixtures to have a lower vapour pressure than predicted by Raoult's Law.

In this chapter we will show such expectations to be incorrect. A vapour pressure: composition study on liquid binary mixtures of $SiCl_4$ or $GeCl_4$ with a range of Lewis bases known to coordinate with $SnCl_4$ showed positive deviations from ideality for all but the strongest base (tetrahydrofuran) with the strongest Lewis acid ($GeCl_4$), rather than the negative deviation had there been significant attraction between the Lewis acid and Lewis base.

These results will be discussed in terms of the energetics involved in adduct formation and the difficulties encountered in comparisons of Lewis acidity or basicity. Finally, as an extension to the main work, we will test the method to see if the degree of deviation for a single acid can be used as a measure of relative Lewis basicity for a wide range of bases.

3.2 Experimental

3.2.1 Reagents

The Group IV halides were purified by vacuum distillation into a trap cooled to -96°C in order to separate hydrogen chloride. The Lewis bases were dried as outlined in Appendix B.

3.2.2 Vapour Pressure measurements

Rigorously anhydrous conditions were employed throughout the experiment by working under dry nitrogen or by standard vacuum line techniques. Vapour pressures were determined manometrically. Acid-base mixtures were prepared by distilling weighed portions of base into a 100ml flask containing a measured quantity of the acid and the vapour pressures of such mixtures were measured at repeated intervals after the liquid mixtures had been stirred vigorously at 0°C. The values reported are constant equilibrium values normally reached after about 1hr. stirring at 0°C. Reproducibility was checked by conducting independent runs with overlapping compositions and starting with fresh batches of MCl_4. Great care was taken to avoid the accumulation of volatile by-products such as hydrogen chloride (from partial hydrolysis) and ethyl chloride. Silicon tetrachloride with diethyl ether is known to react very slowly at room temperature to give $SiCl_3OEt$ and $EtCl$[19]. Monitoring for volatile contaminants, performed by taking the gas phase infra-red spectra of the vapour samples, was maintained throughout each run.

The mixtures were then expanded into a line of known volume estimated to contain about ½g. of typical vapour (about 3l.). Since we required that the composition of the liquid phase should not change by <u>not more</u> than 5% during collection of the vapour this dictated that the total quantity of acid and base should be about 20g. The partial pressures of acid and base in the vapour samples were measured by determining the vapour density and calculating the apparent molecular weight of the vapour which were then used to calculate the mole fractions of acid and base (equation 3.2):

$$M_{app.} = M_L \cdot X_L + M_{MCl_4} \cdot X_{MCl_4} \qquad 3.2$$

where M = molecular weight, X = mole fraction, L = Lewis base and $MCl_4 = SiCl_4$ or $GeCl_4$. The partial pressure of base P_L was then calculated from 3.3:

$$P_L = P.X \qquad 3.3$$

where P = the total pressure. This method of determining vapour pressures relies on there being negligible interaction of the components in the gas phase. Therefore the reliability of the method was established by checking it on totally gaseous mixtures made from known quantities of L and MCl_4. The total pressure was found to be the sum of the partial pressures to within ± 1%.

An alternative method of determining P_L in the ACN/MCl_4 systems was also tried. The intensities of the absorptions in the vapour samples due to the vinyl twist and wag at 960 cm^{-1} and 690 cm^{-1} respectively were measured. However this method proved inadequate since on checking it was found that the band intensities in gaseous ACN were enhanced simply by the addition of a small amount of gaseous MCl_4.

3.3 Results

The complete results for the ten binary systems studied are given in Tables 3.1-3.10 and the vapour pressure composition curves in Figures 3.1-3.5. Table 3.11 summarizes the deviations from ideality for all the Lewis bases studied by listing (i) the experimentally observed vapour pressure, $P_{expt.}$ of 1:1 mixtures of MCl_4 and Ligand, (ii) the vapour pressures P_{ideal} expected for ideal 1:1 mixtures and (iii) the percentage deviation given by equation 3.4:

$$\text{Percentage Deviation} = 100\ \frac{(P_{expt.} - P_{ideal})}{P_{ideal}} \qquad 3.4$$

All nitrile systems, both those studied throughout the composition range (MeCN and ACN), and also those studied

TABLE 3.1 Partial Vapour Pressure Data for System: $SiCl_4$+ACN

Mole % ACN	Wt. Condensate	T°K	Total P mm Hg	Apparent M.W.	Partial P.ACN/mmHg
1.30	1.9246	291	83.41	155.8	10.09
3.35	2.0212	291	87.37	156.2	10.31
6.14	2.0422	293	90.88	152.8	13.36
9.35	2.1000	294.5	97.55	147.1	19.06
12.34	2.0132	295	96.10	143.4	21.82
15.84	1.9153	295	95.36	141.1	23.55
42.19	1.9166	297	93.98	140.5	23.64
67.57	1.8993	296	92.25	141.4	22.51
74.69	1.7026	296	86.26	135.5	25.37

TABLE 3.2 Partial Vapour Pressure Data for System: $GeCl_4$+ACN

Mole % ACN	Wt. Condensate	T°K	Total P mm Hg	Apparent M.W.	Partial P.ACN/mm Hg
1.23	.7551	297	32.75	158.9	11.26
3.56	.9173	297	36.96	171.0	9.90
5.30	.8764	297	38.85	155.5	14.13
6.79	.8459	296	40.82	142.4	18.20
10.02	.9787	295	44.68	149.9	17.82
11.88	.8710	295	44.27	134.7	21.80
16.01	.8571	295	45.58	128.7	24.20
19.91	.8594	295	45.70	128.7	24.22
27.80	.8026	295	46.59	117.9	27.81
32.23	.7821	295	46.82	114.4	29.02
40.7	.7839	295	46.88	115.2	28.60
66.78	.7449	295	43.42	117.3	26.13
83.62	.6998	294	44.30	107.8	29.23
0	-	-	28.54	-	-

TABLE 3.3 Vapour Pressure Data for System: $SiCl_4$ + MeCn

Mole % MeCN	Wt. Condensate	T/K	Total P mm Hg	Apparent M.W.	Partial MeCN/mm Hg
2.36	2.5896	293	82.21	165.09	3.07
5.78	2.7135	293	90.70	156.80	9.20
10.85	2.8446	292.5	98.42	151.27	14.23
15.50	2.8514	292	99.22	150.10	15.24
24.70	2.8385	292	99.72	148.68	16.42
35.43	2.8156	292.5	99.62	147.93	16.98
58.84	2.7999	292.5	100.20	147.02	17.80
70.21	2.7690	291	98.74	146.00	18.31
82.60	2.7107	293.5	98.97	143.84	20.0
89.87	2.9727	293	75.47	137.09	19.22
93.56	1.5963	292.5	63.94	130.67	19.5
96.23	1.2572	293	56.15	117.47	22.85
100.00	-	-	22.83	-	22.83
0	-	-	76.90	-	-

TABLE 3.4 Vapour Pressure Data for System: $GeCl_4$ + MeCN

Mole % MeCN	Wt. Condensate	T/K	Total P. mm Hg	Apparent M.W.	Partial MeCN/mm Hg
4.30	1.3338	296.3	35.28	170.33	8.97
7.35	1.2668	296.5	42.20	159.21	13.43
11.56	1.2655	296.5	46.71	143.69	19.05
25.65	1.2544	296.5	46.69	142.49	19.36
39.30	1.2310	296.3	46.46	140.43	19.82
58.07	1.2075	296.6	46.37	138.16	20.40
71.93	1.2045	296.4	46.40	137.63	20.55
84.09	1.1429	296.3	44.81	135.18	20.48
91.40	1.0101	296.3	41.75	128.23	20.75
95.75	0.7075	296.0	35.78	104.70	22.64
0	-	-	24.30	-	-
100	-	-	23.43	-	-

TABLE 3.5 Vapour Pressure Data for System: $SiCl_4 + Et_2O$

Mole % Et_2O	Wt. Condensate	T/K	Total P mm Hg	Apparent M.W.	Partial Et_2O/mm Hg
10.04	1.1683	295.8	40.33	153.28	17.60
11.50	1.1844	295.2	42.50	147.16	20.40
13.42	1.2590	295.5	45.96	144.80	22.83
15.55	1.3001	297.0	50.36	137.15	27.79
22.34	1.5507	295.2	62.92	130.14	37.86
29.45	1.5591	295.2	72.03	114.30	51.50
32.06	1.5560	295.6	75.12	109.52	56.27
34.62	1.6151	295.6	79.00	108.10	59.98
48.78	1.9005	294.7	102.00	98.22	84.64
57.40	1.9485	294.5	115.02	89.24	102.82
66.55	2.1894	294.7	131.03	88.08	118.22
74.00	2.4009	296.5	145.06	87.78	131.18
81.00	2.4220	296.0	155.20	82.63	146.06
87.40	2.5242	296.0	164.98	81.01	157.18
93.86	2.4732	296.0	172.88	75.75	171.20
0	-	-	24.3	-	-
100	-	-	183.23	-	-

TABLE 3.6 Vapour Pressure Data for System: $GeCl_4 + Et_2O$

Mole % Et_2O	Wt. Condensate	T/K	Total P mm Hg	Apparent M.W.	Partial P Et_2O/mm Hg
10.17	2.4376	295.6	91.75	140.48	28.18
15.90	2.5054	296.0	99.06	133.91	37.23
21.30	2.5231	294.8	106.00	125.52	49.11
33.15	2.8711	295.1	122.50	123.72	59.06
46.59	2.8650	294.8	135.80	111.25	83.15
58.75	2.9087	294.7	149.74	102.40	105.53
71.35	2.8720	295.9	161.29	94.25	127.39
81.90	2.8473	296.4	175.12	86.21	153.01
87.02	2.8704	296.0	179.50	84.67	159.73
96.06	2.7384	296.0	181.66	79.81	170.87
0	-	-	76.90	-	-
100	-	-	183.23	-	-

TABLE 3.7 Vapour Pressure Data for System: $SiCl_4$ + EtOAc

Mole % EtOAc	Wt. Condensate	T/K	Total P mm Hg	Apparent M.W.	Partial P EtOAc/mm Hg
11.45	2.4038	288.0	76.20	162.50	6.89
16.81	2.3864	289.0	76.00	162.32	7.04
24.57	2.3220	290.0	75.38	159.79	9.31
36.00	2.2270	288.0	72.70	157.81	10.75
45.27	2.0545	292.0	70.19	152.88	14.60
58.33	1.8046	292.6	63.50	148.74	16.43
71.50	1.5561	292.3	56.40	144.26	17.70
82.40	1.2666	293.5	49.55	134.20	19.46
89.40	0.9318	292.5	38.85	125.50	21.10
97.01	0.6017	292.6	29.91	105.29	23.63
100	-	-	24.10	-	-
0	-	-	76.79	-	-

TABLE 3.8 Vapour Pressure Data for System: $GeCl_4$ + EtOAc

Mole % EtOAc	Wt Condensate	T/K	Total mm Hg	Apparent M.W.	Partial P EtOAc/mm Hg
6.99	1.0888	291.0	27.71	204.53	2.17
16.39	1.0422	291.3	28.79	188.63	5.87
25.72	1.0155	291.3	30.01	176.32	9.05
40.25	1.0082	291.7	30.91	170.19	10.82
54.50	1.0017	292.7	31.51	165.87	12.11
65.43	0.8927	292.1	31.29	149.07	16.18
83.47	0.6777	292.1	28.03	125.85	19.66
92.05	0.5871	291.0	27.27	112.45	22.02
100	-	-	24.10	-	-
0	-	-	24.30	-	-

TABLE 3.9 Vapour Pressure Data for System: $SiCl_4$ + THF

Mole % THF	Wt. Condensate	T/K	Total P mm Hg	Apparent M.W.	Partial P THF/mm Hg
7.70	2.4200	292.0	76.87	164.43	4.30
18.71	2.3515	292.0	77.20	159.09	8.53
33.09	2.1125	292.0	74.25	148.61	16.16
52.60	1.7098	292.0	69.25	128.96	28.29
65.57	1.4430	292.0	64.17	117.86	34.15
77.01	1.3237	292.1	62.84	110.06	38.46
85.54	1.1439	292.1	59.26	100.86	41.84
91.20	1.0045	292.6	56.97	92.28	45.22
95.08	0.8498	292.1	54.23	81.88	48.82
100	-	-	50.29	-	-
0	-	-	76.90	-	-

TABLE 3.10 Vapour Pressure Data for System: $GeCl_4$ + THF

Mole % THF	Wt. Condensate	T/K	Total P mm Hg	Apparent M.W.	Partial P THF/mm Hg
7.88	0.9664	293.0	25.00	202.60	2.07
14.89	0.9686	293.0	28.91	188.65	4.87
25.93	0.9174	294.2	28.72	168.10	9.35
37.07	0.9576	293.3	31.50	159.49	12.16
47.75	0.8740	293.3	32.60	140.66	16.90
57.88	0.8246	293.0	35.47	122.13	23.00
68.88	0.7143	294.0	38.54	97.13	34.77
82.14	0.6787	294.3	42.67	83.72	39.19
94.53	0.7372	291	48.64	78.79	46.32
100	-	-	50.29	-	-
0	-	-	24.30	-	-

TABLE 3.11 Physicochemical Data for the GpIV Chlorides

Metal	Sn	Si		Ref.
Electronegativity (Pauling)	1.72	2.02	1.74	25
d(M-Cl) (pm)	231	208	201	26,27,28
ΔHf(Sn-Cl) (Kj mol^{-1})	414	343	476	25
ΔHg coord (kJ mol^{-1}) MCl_4.2py	100	83	76	15
ΔHf coord (kJ mol^{-1}) MCl_4.2iq	95	85	75	15

TABLE 3.12 Degree of Deviation for 1:1 mixtures of Lewis Base and $SiCl_4$ at 0°C

Lewis Base^{+}	Pressure observed/ mm Hg	Pressure Ideal/ mm Hg	% Deviation*
Me_3N	336	380	-12
Et_2O	142	130	9
THF	70	64	9
$POCl_3$	56	48	17
EtOAc	68	50	36
ACN	97	55	76
PhCN	69	37	86
MeCN	100	50	100
EtCN	107	46	133

+ In order of predicted basicity. Pyridine and Me_2SO were also studied but undergo chemical reactions with $SiCl_4$

* % Deviation = $$\frac{P_{obs} - P_{id}}{P_{id}} \times 100$$

Figure 31.a, $SiCl_4$ - CH_2CHCN

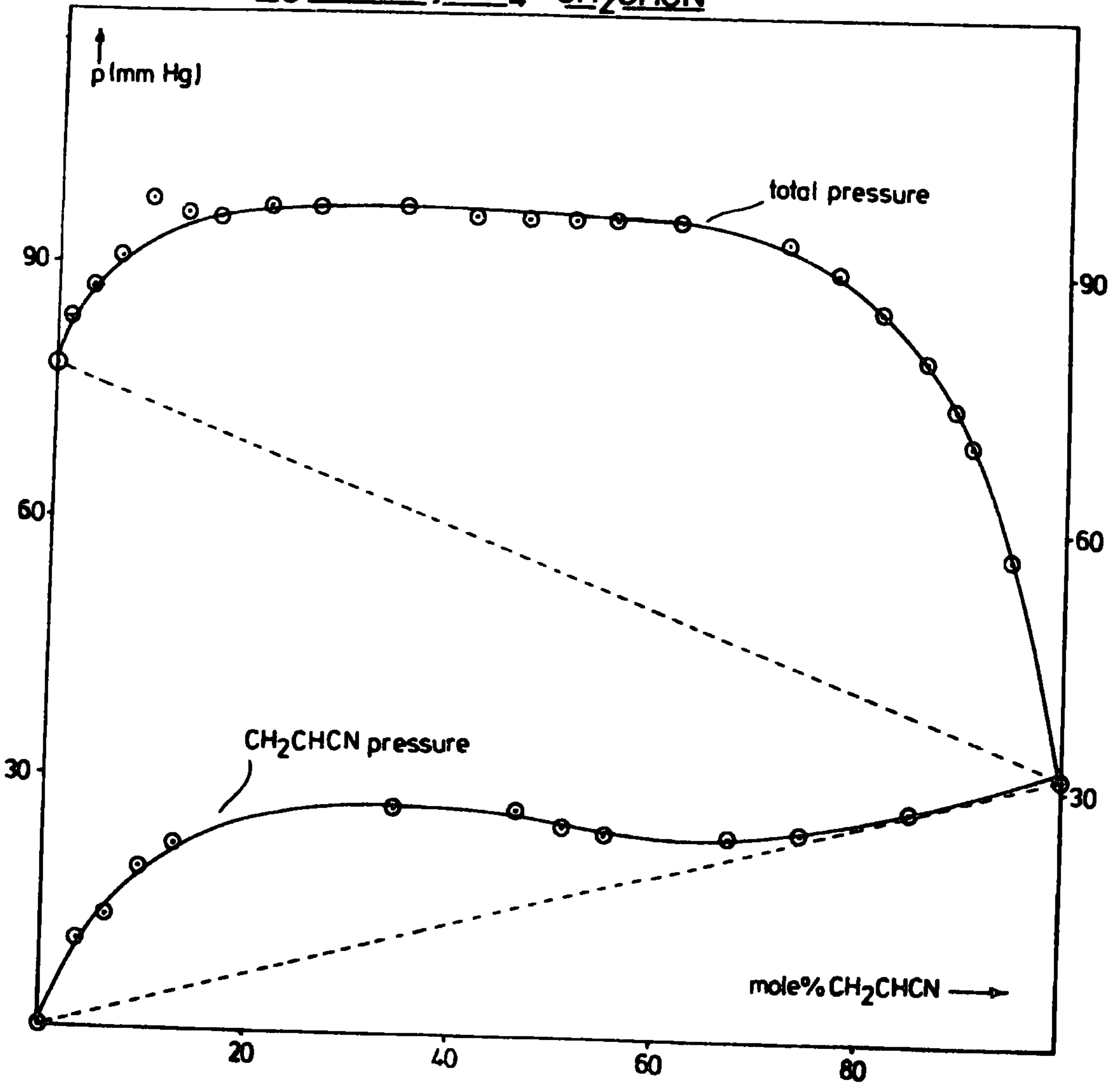


Figure 3.1.b GeCl$_4$-CH$_2$CHCN

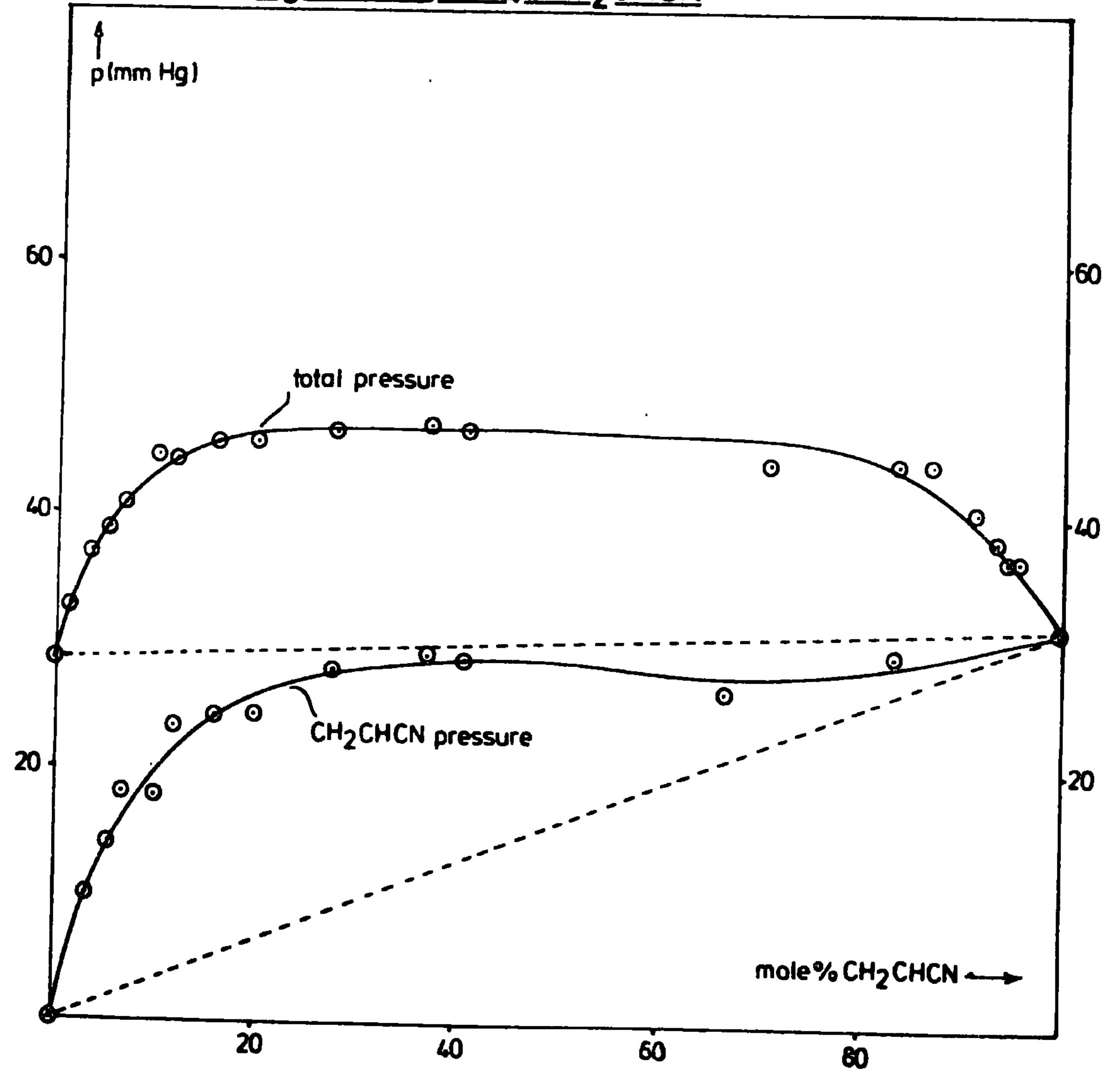


Figure 3.2a, SiCl4 -MeCN

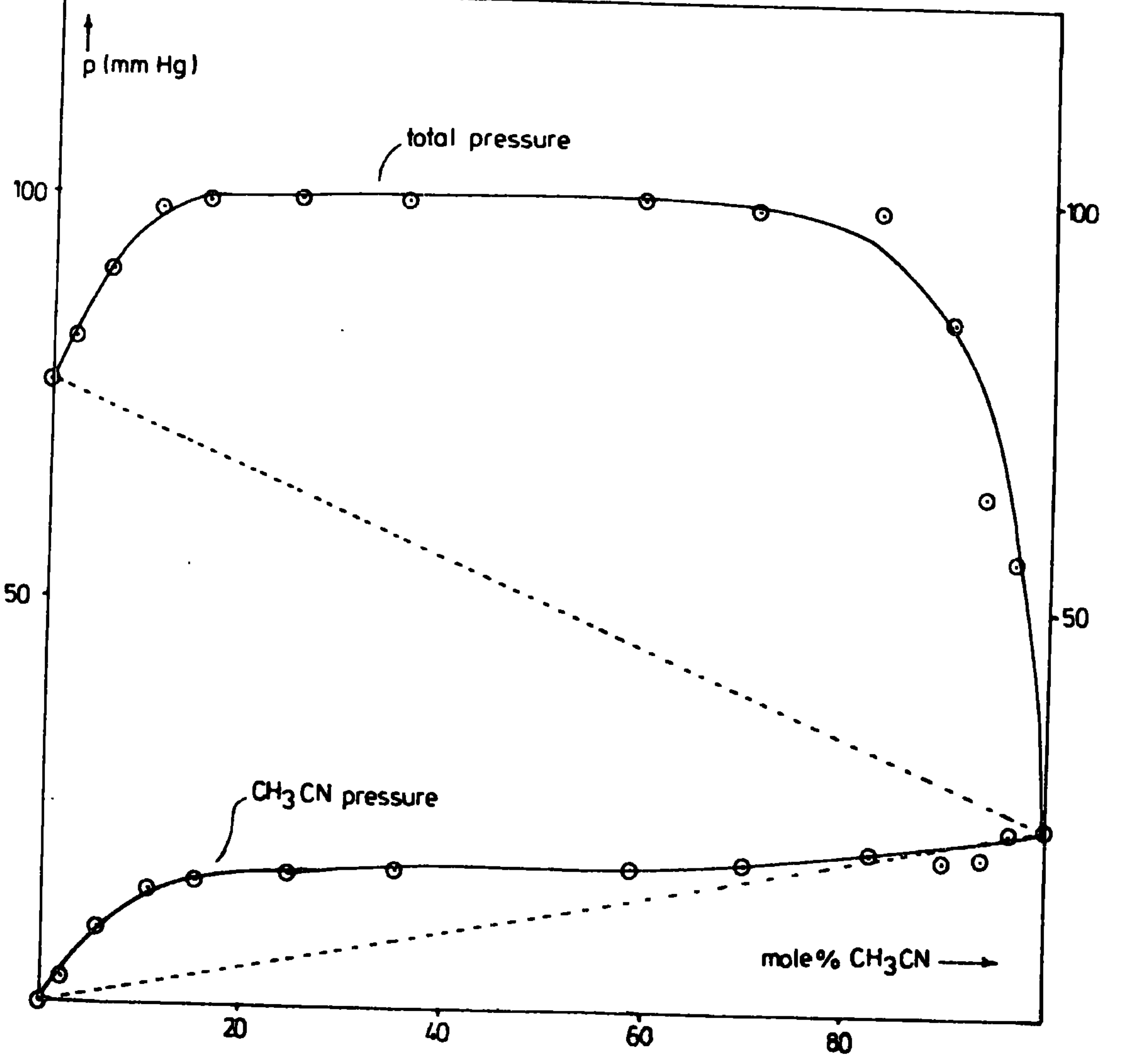


Figure 3.2.b, $GeCl_4$ - MeCN

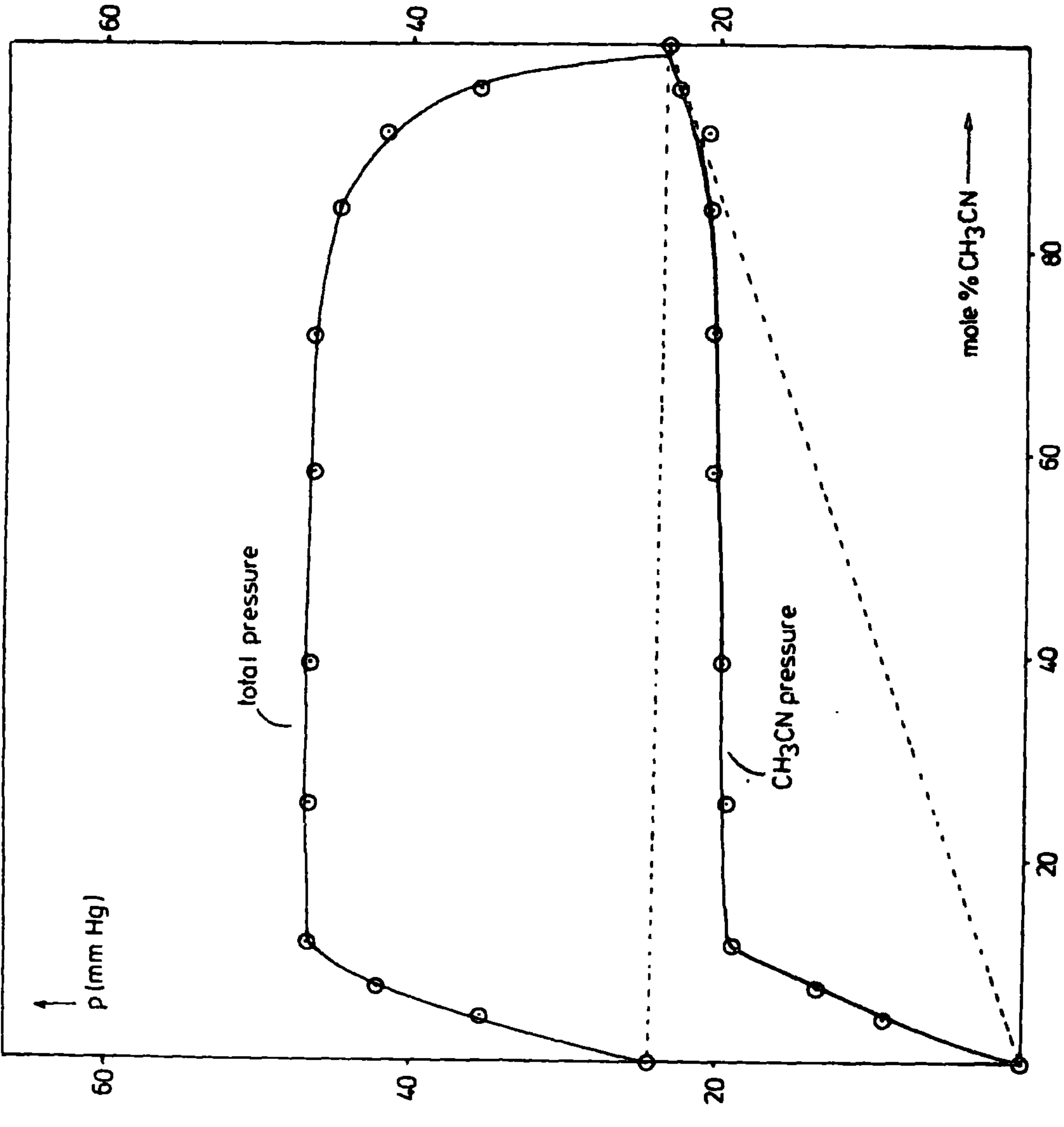


Figure 3.3a, $SiCl_4$-$MeCO_2Et$

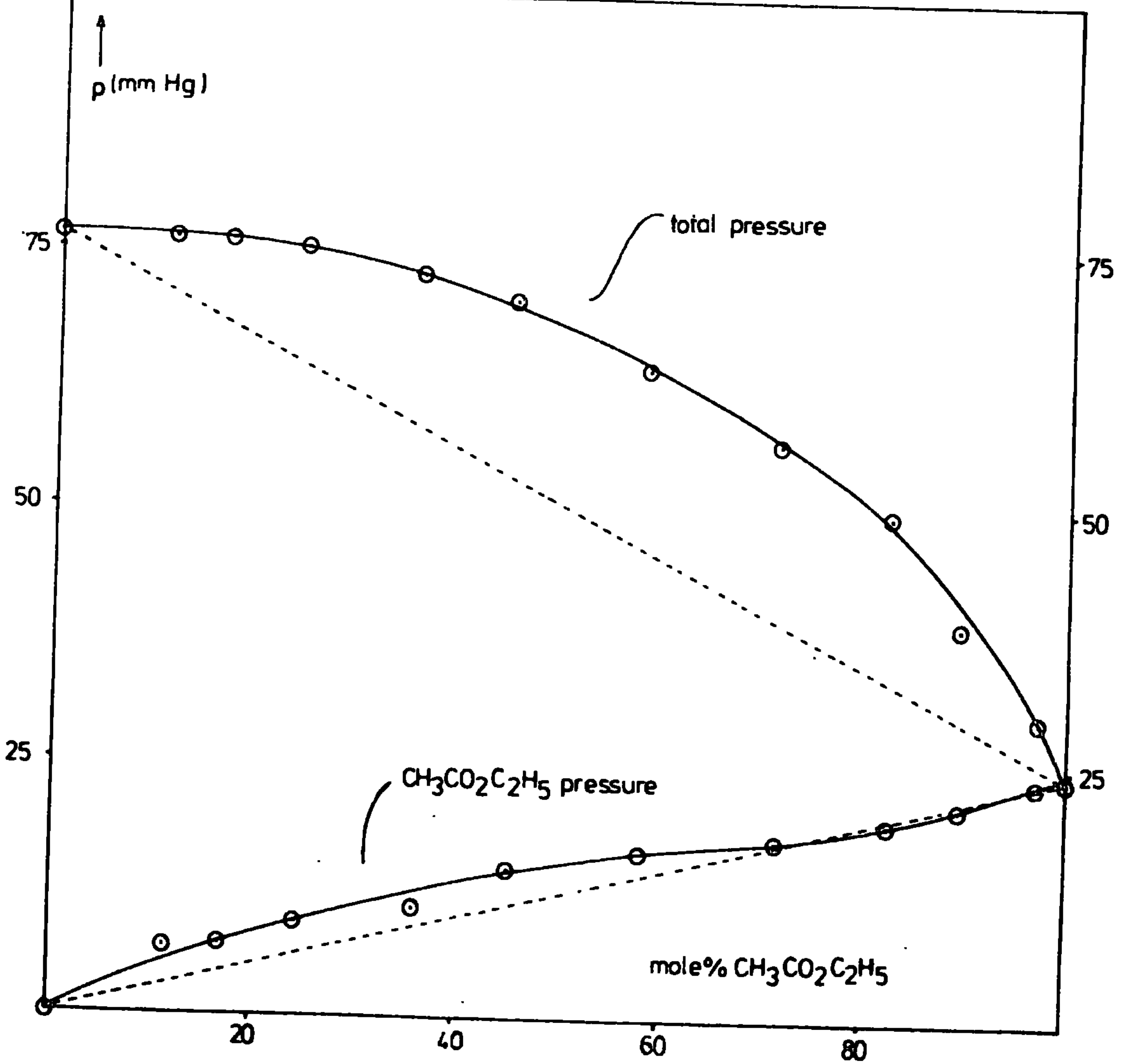


Figure 3.3b: $GeCl_4$-$MeCO_2Et$

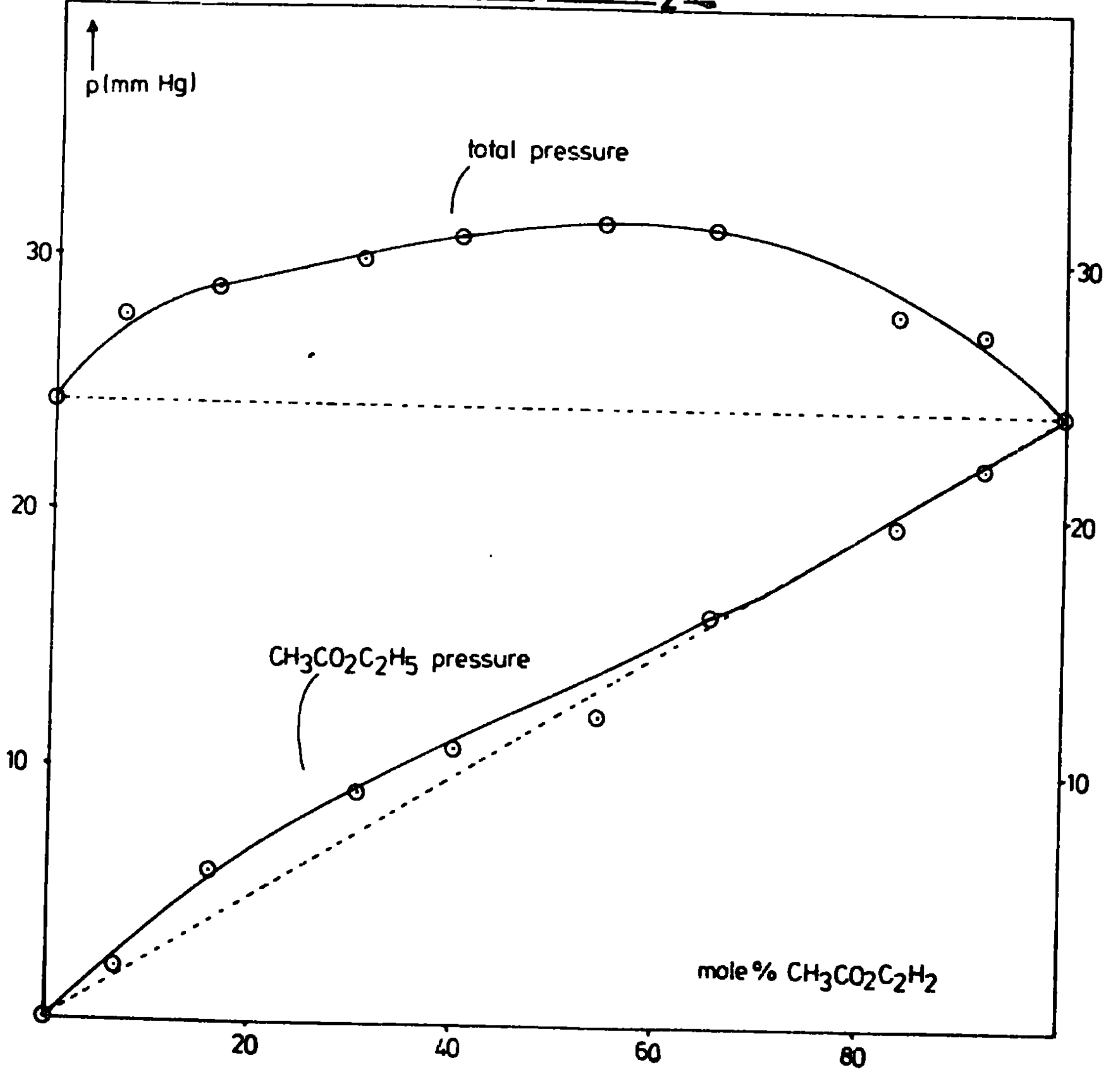


Figure 3.4.a. $SiCl_4$- Et_2O

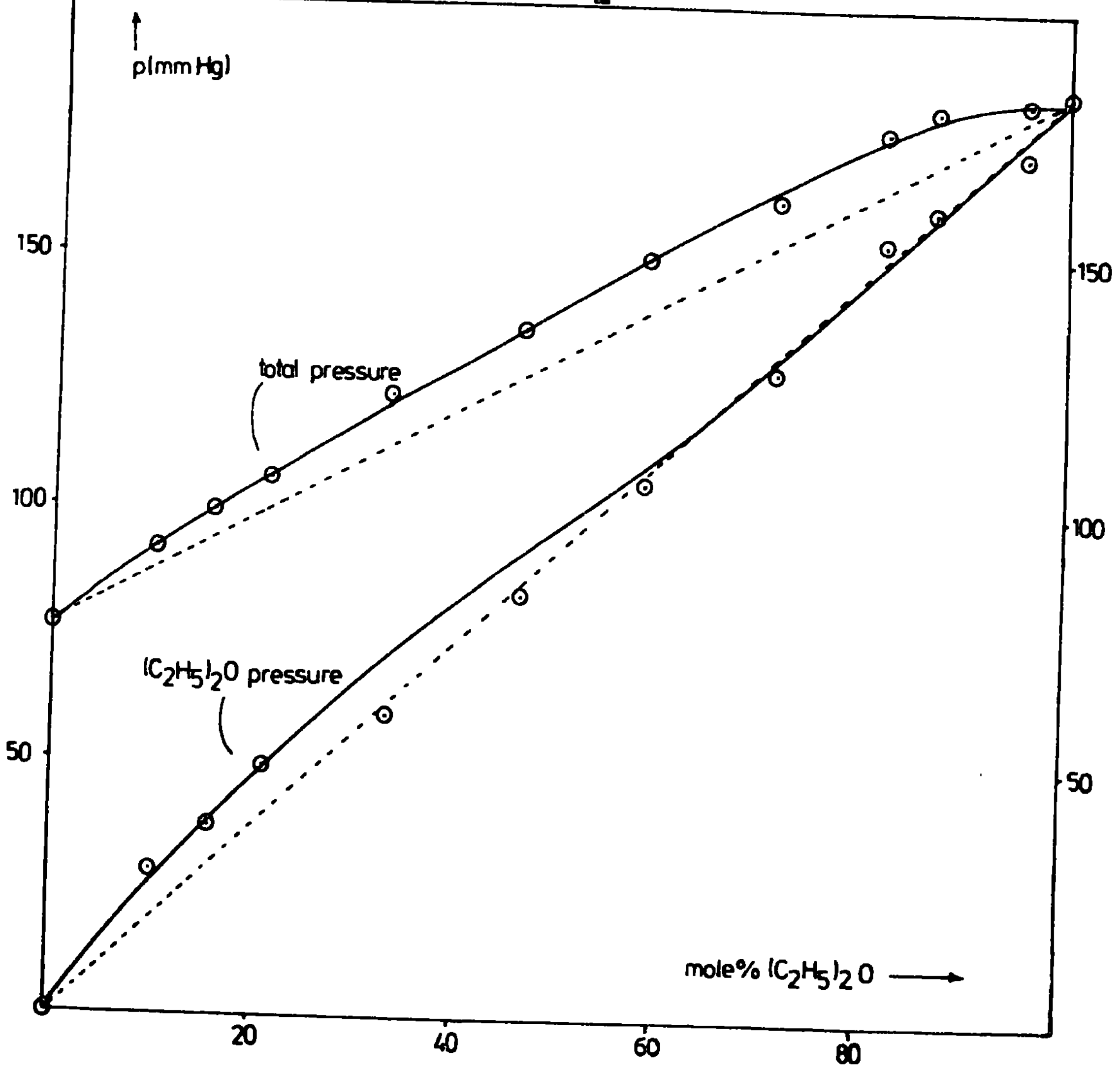


Figure 3.4.b, $GeCl_4$-Et_2O

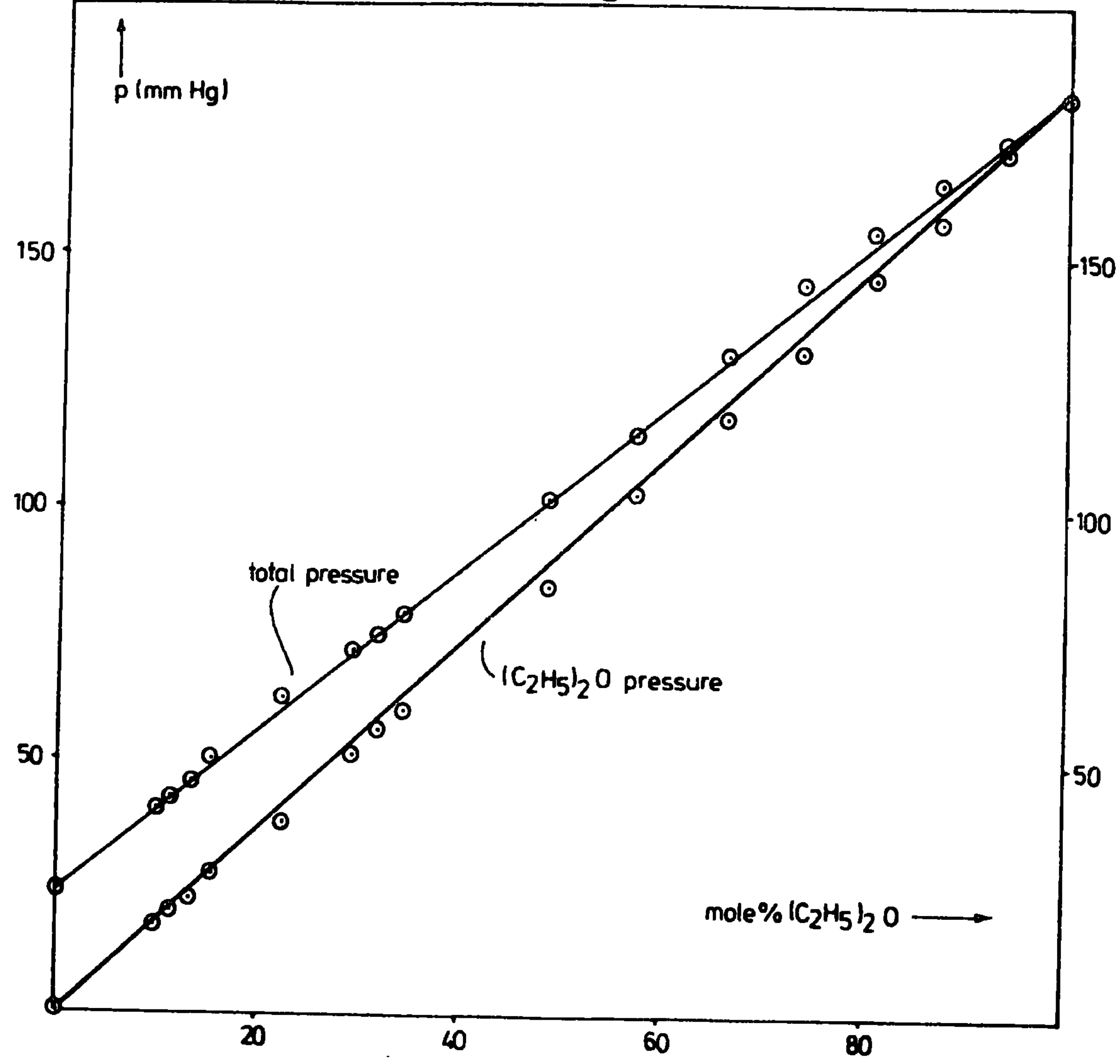


Figure 3.5.a, $SiCl_4$-THF

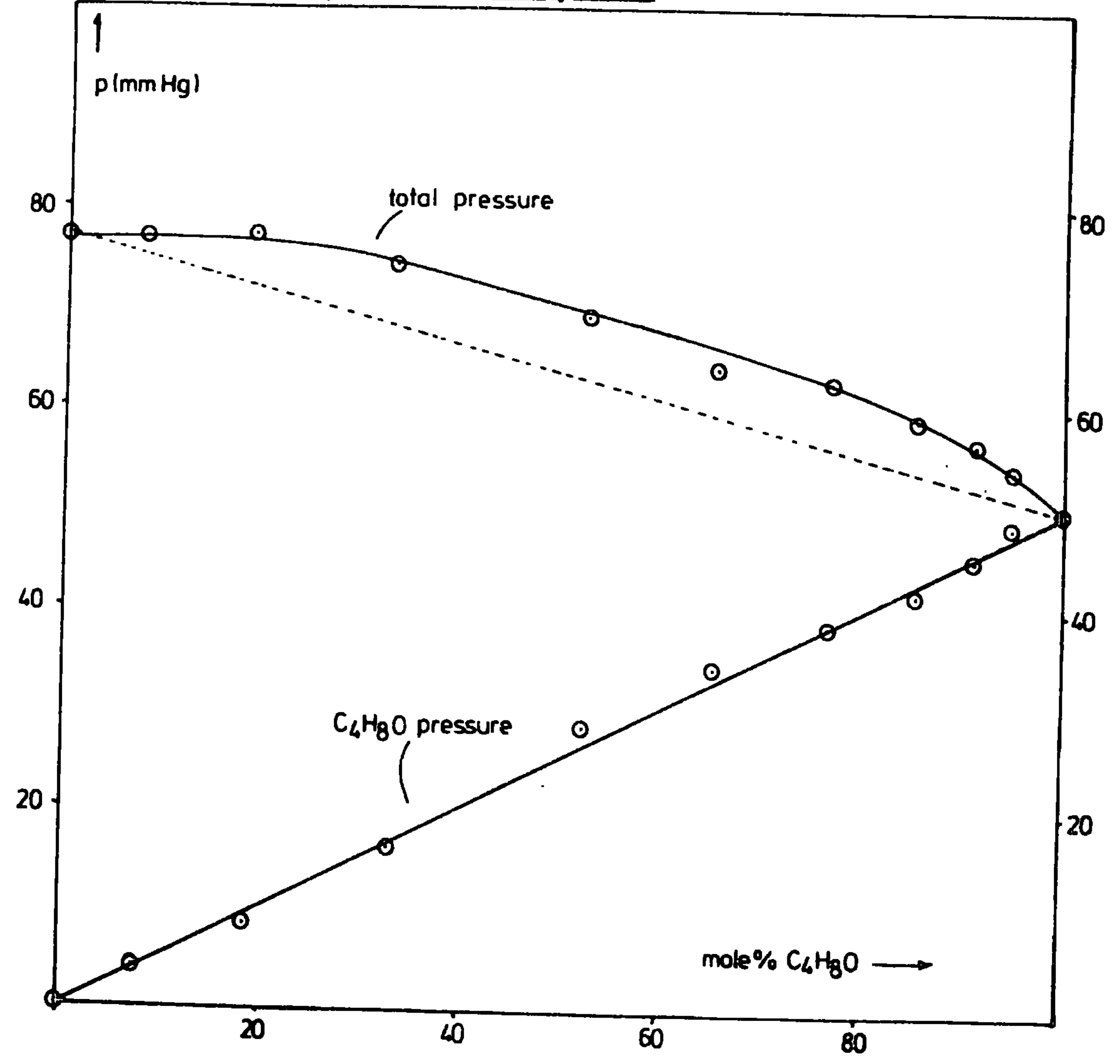
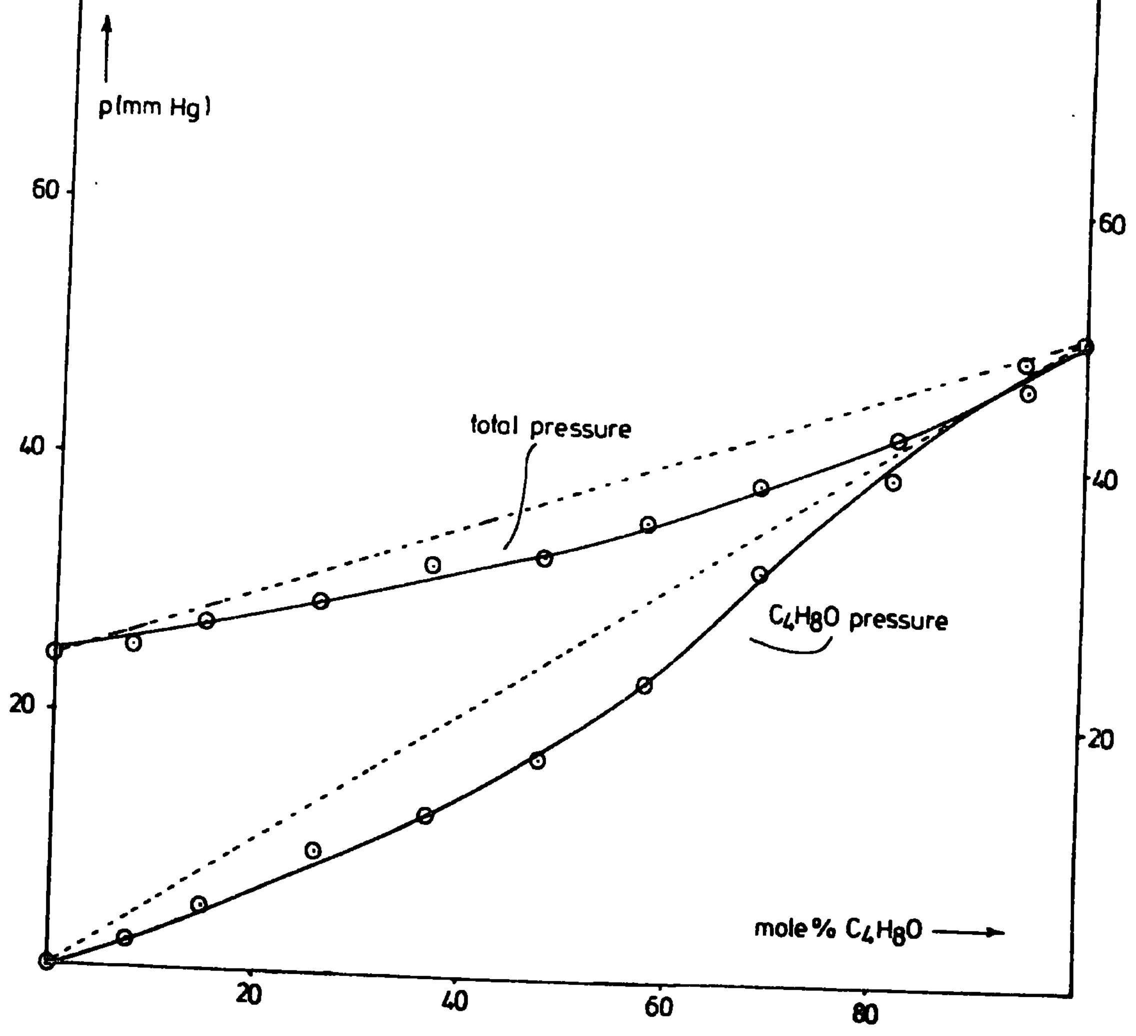


Figure 3.5.b, $GeCl_4$ - THF



only as 1:1 mixtures show pronounced positive deviations from ideality. The nitriles ACN and MeCN differ in their behaviour towards $SiCl_4$ and $GeCl_4$ in that whilst ACN is miscible with both acids throughout the composition range, acetonitrile and MCl_4 form two liquid phases at 0°C over the approximate ranges 15-80 mole % (M=Si) and 10-70 mole % (M=Ge). Between these limits the vapour pressures correspond to saturated solutions of MeCN in MCl_4. (The Group IV chloride is more volatile in both the ACN systems although it is somewhat marginal for MeCN).

Both ethyl acetate systems, Figures 3.3a,b, show positive deviations from ideality although the deviations are significantly less than in the nitrile systems.

Towards ethers, Et_2O and THF, the different affinities of $SiCl_4$ and $GeCl_4$ reflect the greater Lewis acidity of the latter. So whilst $SiCl_4$ and Et_2O show a slight positive deviation from ideality $GeCl_4$ and Et_2O exhibit near ideal behaviour (Figures 3.4a,b). With tetrahydrofuran the slight positive deviation shown by $SiCl_4$ is contrasted by a slight negative deviation by $GeCl_4$.

3.4 Discussion

All five bases studied throughout the composition range are known to form stable adducts with tin tetrachloride.[5,6,7,10,11,14,15] These results therefore confirm the established gradation of Group IV Lewis acids $SiCl_4 < GeCl_4 < SnCl_4$. We consider that qualitatively the results are also consistent with increasing donor character towards MCl_4 in the sequence MeCN < ACN < $MeCO_2Et$ < Et_2O < THF. Positive deviations from ideality in $SiCl_4$-ether and $SiHCl_3$-ether systems have been observed in the attempted separation of these Lewis acids[20] although the implications were not commented upon. Other previous phase studies have attempted to interpret information from the solid   liquid phase transition as in the case of early studies on ether systems[10,11] or more recently on $POCl_3$-MCl_4 systems[21,22,23]. If the interactions in the solid are not well established (e.g. crystal structure or lattice energy data) it is difficult to interpret results from such studies in terms of the attractive or repulsive nature of the interaction in the liquid phase.

The absence of negative deviation may be rationalized as follows.

In order to form an adduct, $MCl_4.L$, it is necessary for the Group IV tetrahalide to change from a tetrahedral to a pseudopyramidal arrangement to accommodate the ligand and allow the dative bond L ⟶ M to form, Figure 3.6, since in

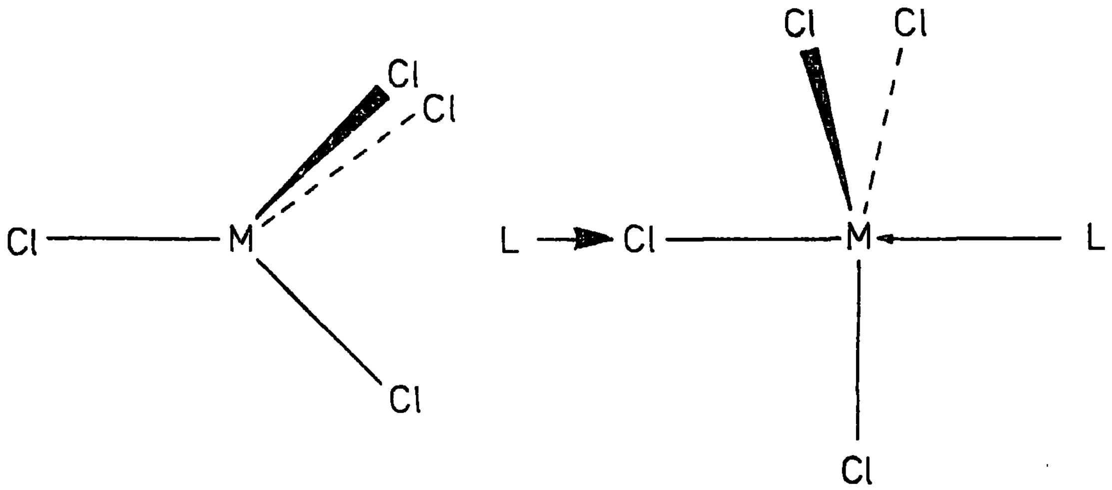


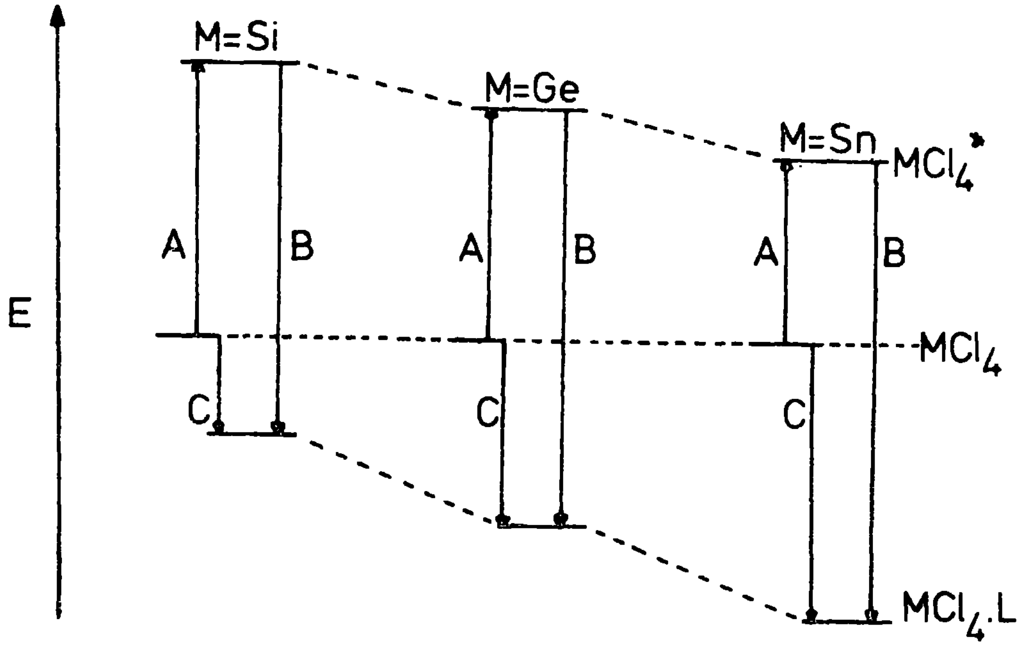
Figure 3.6

their uncoordinated form the tetrachlorides have insufficient space between the chlorine atoms to allow access of L to M without distortion. The space between the chlorine atoms has a diameter of 24pm in $SiCl_4$, 32pm in $GeCl_4$ and 80pm in $SnCl_4$. Thus the energy necessary to deform $SiCl_4$ and $GeCl_4$ will be considerably greater than for $SnCl_4$. Therefore unless the energy of the new $L \longrightarrow M$ bond, $E(L \longrightarrow M)$, exceeds the reorganization energy, ΔH_{reorg}, needed to deform MCl_4, adduct formation will not occur and liquid mixtures of MCl_4 and L will then have a Vapour pressure that reflects the lack of affinity that non-polar pseudospherical MCl_4 molecules have for non-spherical base molecules.

Figure 3.7 illustrates qualitatively the difference between $SiCl_4$, $GeCl_4$, and $SnCl_4$ in their behaviour towards a strong Lewis base such as pyridine with which all three Lewis acids form adducts. The enthalpy change, ΔH_{coord}, for the coordination reaction 3.5, becomes progressively less exothermic in the sequence Sn>Ge>Si (as shown in Table 3.12)

$$MCl_4 + 2L \longrightarrow MCl_4.2L \qquad 3.5$$

Figure 3.7
Enthalpy changes in the formation of $MCl_4.L$



MCl_4^*=the reorganised [trigonal pyramidal] MCl_4 molecule

$A=\Delta H_{reorg}$

$B=E[L\rightarrow M]$

$C=\Delta H_{coord}$

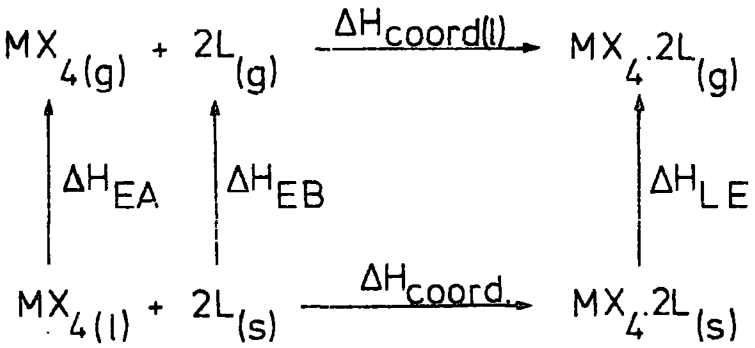
This enthalpy change, ΔH_{coord}, probably represents the difference between E(L ⟶ M), (expected from increasing electronegativity to change in the sequence $SnCl_4 > GeCl_4 > SiCl_4$ (Table 3.11) and ΔH_{reorg} (expected to decrease as the M-Cl bonds get longer and weaker (Table 3.12) in the sequence $SiCl_4 > GeCl_4 > SnCl_4$).

Stepwise changes in going from $SnCl_4$ to $GeCl_4$ and from $GeCl_4$ to $SiCl_4$ are not constant between Lewis bases. For example when the ligand in question is pyridine the steps are 17 kJ mol^{-1} and 7 kJ mol^{-1} respectively. Whereas with isoquinoline the steps are 10 kJ mol^{-1} and 6 kJ mol^{-1} respectively. Nevertheless it is apparent that unless the formation of a tin IV chloride adduct involves the formation of <u>at least</u> some 20 kJ mol^{-1} and probably considerably more than the formation of adducts with $GeCl_4$ and $SiCl_4$ is unlikely.

The binary systems $SiCl_4$/L and $GeCl_4$/L where L=THF or ethyl acetate, show nearly ideal behaviour. (Since non-interacting dissimilar molecules such as $SiCl_4$ and hexane[24] show a positive deviation it would appear reasonable to assume that this is a genuine feeble association). The reported values of H_{coord} for the formation of $SnCl_4.2EtOAc$ and $SnCl_4.2THF$[12] are 44 kJ mol^{-1} and 59 kJ mol^{-1}. Therefore it seems likely a negative deviation from Raoult's Law can only be expected if the base when mixed with $SnCl_4$ evolves about 50-60 kJ mol^{-1}.

However a note of caution is necessary here, one which will to some extent reconcile the different limiting values for prediction of a negative deviation estimated above.

All the available thermochemical data for these systems is concerned with solid addition compounds. Consideration of a sample Born-Haber cycle, Figure 3.8, indicates that ΔH_{coord} contains a term due to the lattice energy of the adduct.



ΔH_{EA}=Heat of vapourization of Lewis Acid

ΔH_{EB}=Heat of vapourization of Lewis Base

ΔH_{LE}=Lattice Energy

Figure 3.8

For accurate comparisons to be made one must therefore consider $\Delta H_{coord(g)}$, the heat of formation of the adduct in the gas phase from the cycle:

$$\Delta H_{coord(g)} = +\Delta H_{EA} + 2\Delta H_{EB} + \Delta H_{coord} - \Delta H_{LE} \qquad 3.6$$

Although latent heats of evaporation of Lewis acids and bases are usually known, to find $\Delta H_{coord(g)}$ requires knowledge of the Lattice energy, ΔH_{LE}, a quantity only rarely determined. For this reason one may only compare ΔH_{coord} if the addition compounds are of closely similar structure. This is perhaps an unreasonable assumption to make in this situation and may account for the divergent values estimated for the minimum enthalpy change necessary in the $SnCl_4$:L system for prediction of the behaviour of the $SiCl_4$:L and $GeCl_4$:L binary system.

In view of these limitations placed on interpreting ΔH_{coord} an attempt has been made to quantify the degree of deviation from ideality of 1:1 mixtures of $SiCl_4$ and Lewis base in the hope that this may be a measure of the relative basicity of a range of Lewis bases. Table 3.12 shows the degree of deviation for 1:1 mixtures calculated from

$$\text{Degree of Deviation} = \frac{(\text{Observed Pressure})-(\text{Ideal Pressure})}{(\text{Ideal Pressure})} \times 100$$

The results are not consistent with the established Lewis basicities of several of the bases studied. For instance $POCl_3$, known to be a weak base towards $SnCl_4$ from NQR measurements (Chapter Four), appears as more basic than ethyl acetate. Similarly the method does not discriminate between diethyl ether and the more basic ether, tetrahydrofuran.

3.5 Summary

The extent of difference in the behaviour of tin tetrachloride and germanium and silicon tetrachlorides towards a variety of Lewis bases has been demonstrated by vapour pressure measurements of the liquid binary mixtures. The relative Lewis acidity has been shown to increase in the sequence $SiCl_4 < GeCl_4 << SnCl_4$. The method has circumvented the problems of Lattice energy considerations associated with solid liquid equilibria. An unsuccessful attempt has been made to classify the relative Lewis basicities of the donors by their degree of deviation from ideality.

CHAPTER FOUR

The Study of some Tin IV Chloride Adducts by ^{35}Cl Nuclear Quadrupole Resonance

4.1 Introduction

Of the large number of known tin IV chloride adducts $SnCl_4.2L$ or $SnCl_4.L\text{-}L$[1-3], (L = a monodentate Lewis base, L-L = a bidentate Lewis base) the compounds *cis* $SnCl_4.2L$ (L = Me_2SO[4], MeCN[5], $POCl_3$[5], $SeOCl_3$[7]),*cis* $SnCl_4.\ NC(CH_2)_3CN$[8], and *trans* $SnCl_4.2py$[9] (py = pyridine) have been the subject of X-ray crystallographic studies.

However the stereochemistry has usually been determined from the vibrational spectra of the compounds[10-16] although it has been pointed out[12,13] that this method may lead to erroneous conclusions if the absorption bands have merged or solid state effects have caused band splitting. The Sn-Cl vibrations may also be obscured by other absorptions unless $^{116}Sn\text{-}^{124}Sn$ isotopic enrichment[17,18] is used to aid assignment.

Since ^{35}Cl nuclear quadrupole resonance studies are in principle capable of distinguishing between *cis* and *trans* isomers of $SnCl_4.2L$ or $SnCl_4.L\text{-}L$[19,20] we have recorded the ^{35}Cl NQR spectra of the $SnCl_4.2L$ series for L = MeCN, CH_2:CHCN, Bu^tCN, PhCN, $CH_2(CN)_2$, 1,2 $C_6H_4(CN)_2$ $4MeC_6H_4CH_2CN$, $2MeC_6H_4CH_2CN$, Me_2SO and THT (THT = tetrahydrothiophene, C_4H_8S).

In this chapter we will report the nqr spectra of the above compounds and discuss their structural implications. As a corollary a comparison will be made between the vibrational and nqr spectral methods for the assignment of *cis* or *trans* stereochemistry in pseudo octahedral complexes.

4.1.1 General Principles of N.Q.R.

The fundamental requirements for nuclear quadrupole resonance are:

(1) The sample must contain a quadrupole moment in an unsymmetrical electronic environment.

(2) The effect is only observed in the solid state where the field gradient axes are fixed. In liquids and gases, molecular vibrations and tumbling, which occur on a faster time scale than the radiofrequency timescale average the field gradient to zero.

(3) The chosen nuclear isotope must be in relatively high abundance (i.e.$>$ 20%) and in addition about 2g of crystalline sample are usually required.

The theory of the nuclear quadrupole resonance effect may be explained by considering the way in which the nuclear quadrupole moment interacts with the electronic environment. A quadrupolar nucleus behaves as if it were extended along its axis of spin with the charge either compressed or extended on this axis. A positive moment is represented by a prolate sphere (extension along the spin axis) and a negative moment by an oblate sphere (compression along the spin axis) as shown in Figure 4.0.

The magnitude of the quadrupole moment is given by equation 4.1.

$$eQ = \int r^2 \rho (3\cos^2\theta - 1)d\tau \qquad 4.1$$

where e is the absolute charge of an electron, ρ is the charge density in a volume element $d\tau$ at a distance r from the centre and θ is the angle between the nuclear spin axis and the radius vector r. If the nuclear quadrupole is non zero (i.e. the nucleus is not a site of tetrahedral or octahedral symmetry) then the energy of the system will depend on the orientation of the nucleus and there will be

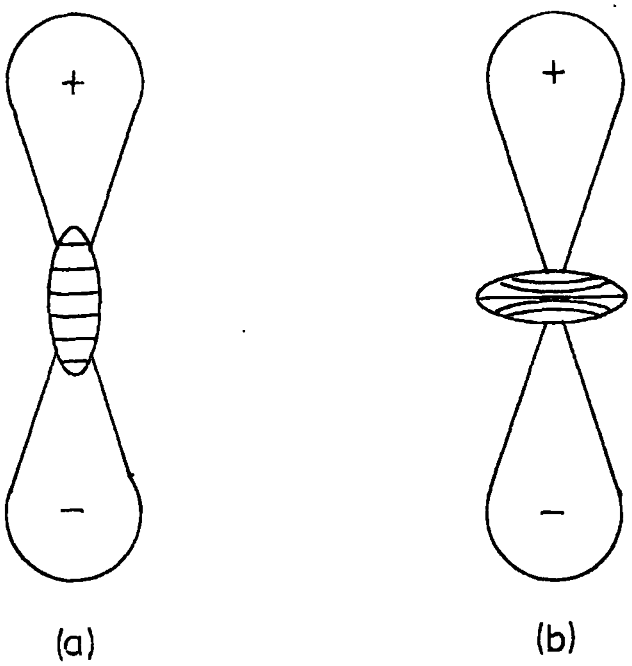


Figure 4.0

a minimum energy for the system. In Figure 4.0.a the energy of interaction will be less since there is less separation of charges and may be considered the ground state whilst 4.0.b is the excited state since energy is required to separate the charges of opposite sign. At the nuclear level the energy levels will be quantized with different orientations giving rise to different energy levels. Transitions are brought about by interaction between the magnetic dipole of the nucleus and an applied magnetic field in the form of radiofrequency electromagnetic radiation. Thus energy levels arise from the *electric* quadrupole interaction with the surroundings whilst the transitions between energy levels arise from *magnetic* dipole interactions with an applied field.

When the electric field gradient is symmetrical about an axis as for instance in a σ bond the energy levels are given by:

$$E = \frac{e^2Qq}{4I(2I-1)}\left[3M_I^2 - I(I+1)\right] \qquad 4.2$$

where eQ is the nuclear quadrupole moment from equation 4.1, eq is the magnitude of the electric field gradient on the symmetry axis, I the nuclear spin quantum number and M_I the nuclear magnetic quantum number which takes the values +I, I-1, ... , -I.

The electric field gradient tensor is defined in a diagonal form so that all off diagonal terms, e.g. $\partial V^2/\partial x\partial y$, are zero when x,y and z are the tensor axes. From the Laplace equation the sum of the field gradients in these directions are zero (equation 4.3).

$$\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2} = 0 \qquad 4.3$$

The axis are defined so that:

$$\frac{\partial^2 V}{\partial z^2} \geqslant \frac{\partial^2 V}{\partial y^2} \geqslant \frac{\partial^2 V}{\partial x^2}$$

and the electric field gradient defined by equation 4.4.

$$\frac{\partial^2 V}{\partial z^2} = eq \qquad 4.4$$

The asymmetry parameter, η, which represents the degree of distortion from axial symmetry of the field gradient as a value from 0-1, is defined as

$$\eta = \left(\frac{\partial^2 V}{\partial x^2} - \frac{\partial^2 V}{\partial y^2}\right) \Bigg/ \frac{\partial^2 V}{\partial z^2} \qquad 4.5$$

When $\partial^2V/\partial x^2$ equals $\partial^2V/\partial y^2$ the field gradient is symmetric and η equals zero.

For nuclei of spin I = $^3/_2$, from equation 4.2, the energy levels are therefore given by:

$$E_{\pm 1/2} = -\ ^1/_4\ e^2Qq$$

$$E_{\pm 3/2} = \ ^1/_4\ e^2Qq \qquad 4.6$$

The selection rule for magnetic dipole transitions is:

$$\Delta M_I = \pm 1$$

and hence only one frequency is observed:

$$\nu = \ ^1/_2\ \frac{e^2Qq}{h} \qquad 4.7$$

The term e^2Qq/h is the nuclear quadrupole coupling constant in units of MHz. If the asymmetry parameter is non-zero the transition frequency is modified to

$$\nu = \ ^1/_2\ \frac{e^2Qq}{h} \left(1 + \frac{\eta^2}{3} \right)^{\frac{1}{2}} \qquad 4.8$$

and the quadrupole coupling constant cannot be derived from ν without knowledge of η. In practice η is small for singly coordinate atom atom such as chlorine and an error in neglecting values of η below 0.1 results in errors of less than 0.16% in the coupling constant, hence the coupling constant is simply twice the resonant frequency.

For further discussion of the theory of the method and applications outside of this Chapter the reader is referred to reference 22.

The method of detecting the resonant frequency is to apply a frequency swept radiofrequency field to coils around the sample contained in a glass vial, all surrounded by a metal can and observe the power absorbed by the sample. Further instrumental details may be found in many of the references cited in this Chapter.

4.2 Experimental

Starting materials were purified as described in Appendix B or by standard techniques.[23] The nitrile adducts $SnCl_4.2RCN$ (R = Me, CH_2:CH, Bu^t, Ph, $2MeC_6H_4CH_2$, $4MeC_6H_4CH_2$) and $SnCl_4.2(NC(CH_2)_3CN)$ were prepared by mixing solutions of the ligand, 45 mmole of ligand in 50ml of toluene, with 20 mmole of $SnCl_4$. The adducts separated as crystals when the solutions were cooled or reduced in volume. After being washed with cold toluene they gave analyses consistent with the formulation.

The dinitrile adducts $SnCl_4.NC(CH_2)_nCN$ n = 1,2,4 and $SnCl_4.2C_6H_4CN_2$ (not the 1:1 adduct) precipitated from solution on mixing equimolar proportions of the compounds in toluene and could not be recrystallized. They were insoluble in aprotic solvents and apparently solvolysed in protic solvents.

The dimethyl sulphoxide adduct was prepared according to the method of Cotton and Francis[24] and recrystallised from hot water. The tetrahydrothiophene (THT) adduct, $SnCl_4.2THT$ was prepared from both chloroform and pentane. The adduct precipitated immediately on addition of THT to a solution of $SnCl_4$ in pentane and could not be recrystallised. It was also prepared by using chloroform as a solvent in which the adduct is very soluble.

Bis Diphenyl methyleneammonium hexachlorostannate IV $(Ph_2CNH_2)_2SnCl_6$, was prepared from $SnCl_4$ and PhCNH in dichloromethane in the appropriate proportions. Analyses for all the compounds are given in Table 4.1.

^{35}Cl nuclear quadrupole resonance spectra were recorded on a commercial Decca mid range spectrometer using Zeeman modulation. The positions of the line centres were determined after side-

TABLE 4.1 Analytical Data for $SnCl_4$ adducts

Compound	Element			
	C*	H*	Cl*	Other*
$SnCl_4$.2MeCN	14.3(14.0)	1.8(1.7)	41.0(4.14)	N:8.4(8.2)
$SnCl_4$.2ACN	19.9(19.6)	1.7(1.6)	39.1(38.7)	N:7.5(7.6)
$SnCl_4$.Bu^tCN	27.5(31.9)	4.1(4.0)	33.9(31.5)	N:6.4(6.2)
$SnCl_4$.2PhCN	35.8(36.0)	2.2(2.1)	32.9(30.4)	N:6.1(6.0)
$SnCl_4$.2(2Me$C_6H_4CH_2$CN)	42.7(41.3)	3.8(3.4)	27.3(27.2)	N:5.3(5.4)
$SnCl_4$.2(4Me$C_6H_4CH_2$CN)	42.5(41.3)	3.7(3.4)	27.4(27.2)	N:5.5(5.4)
$SnCl_4$.2$CH_2(CN)_2$	18.7(18.3)	1.0(1.0)	35.1(36.1)	N:14.9(14.2)
$SnCl_4$.NC$(CH_2)_2$ CN	15.1(14.1)	1.5(1.2)	42.1(41.6)	N:9.3(8.2)
$SnCl_4$.NC$(CH_2)_3$CN	16.8(16.9)	1.7(1.7)	39.0(40.0)	N:8.0(7.9)
$SnCl_4$.NC$(CH_2)_4$CN	19.7(19.5)	2.6(2.2)	39.5(38.5)	N:7.3(7.6)
$SnCl_4$.2($C_6H_4(CN)_2$)	37.0(37.2)	1.4(1.5)	26.2(27.5)	N:11.0(10.8)
$SnCl_4$.2py	29.4(28.6)	3.0(2.4)	33.5(33.9)	N:7.3(6.7)
$SnCl_4$.2Me_2SO	11.0(11.5)	2.9(2.9)	33.7(34.0)	S:15.5(15.4)
$SnCl_4$.2THT[ø]	22.1(22.0)	4.0(3.7)	32.2(32.5)	S:15.1(14.7)
$SnCl_4$.2THT[†]	21.8(22.0)	3.8(3.7)	33.0(32.5)	S:14.6(14.7)
$(Ph_2CNH_2)_2SnCl_6$	46.0(45.1)	2.8(2.9)	30.9(30.8)	N:3.9(4.0)

* Calculated values in parentheses

ø Precipitated from n-pentane

† Prepared in dichloromethane

band suppression. Low temperature spectra were recorded using samples cooled by nitrogen gas evaporating from liquid nitrogen or by standard slush baths. Temperatures were recorded using a comark electronic thermometer and a copper constantan thermocouple.

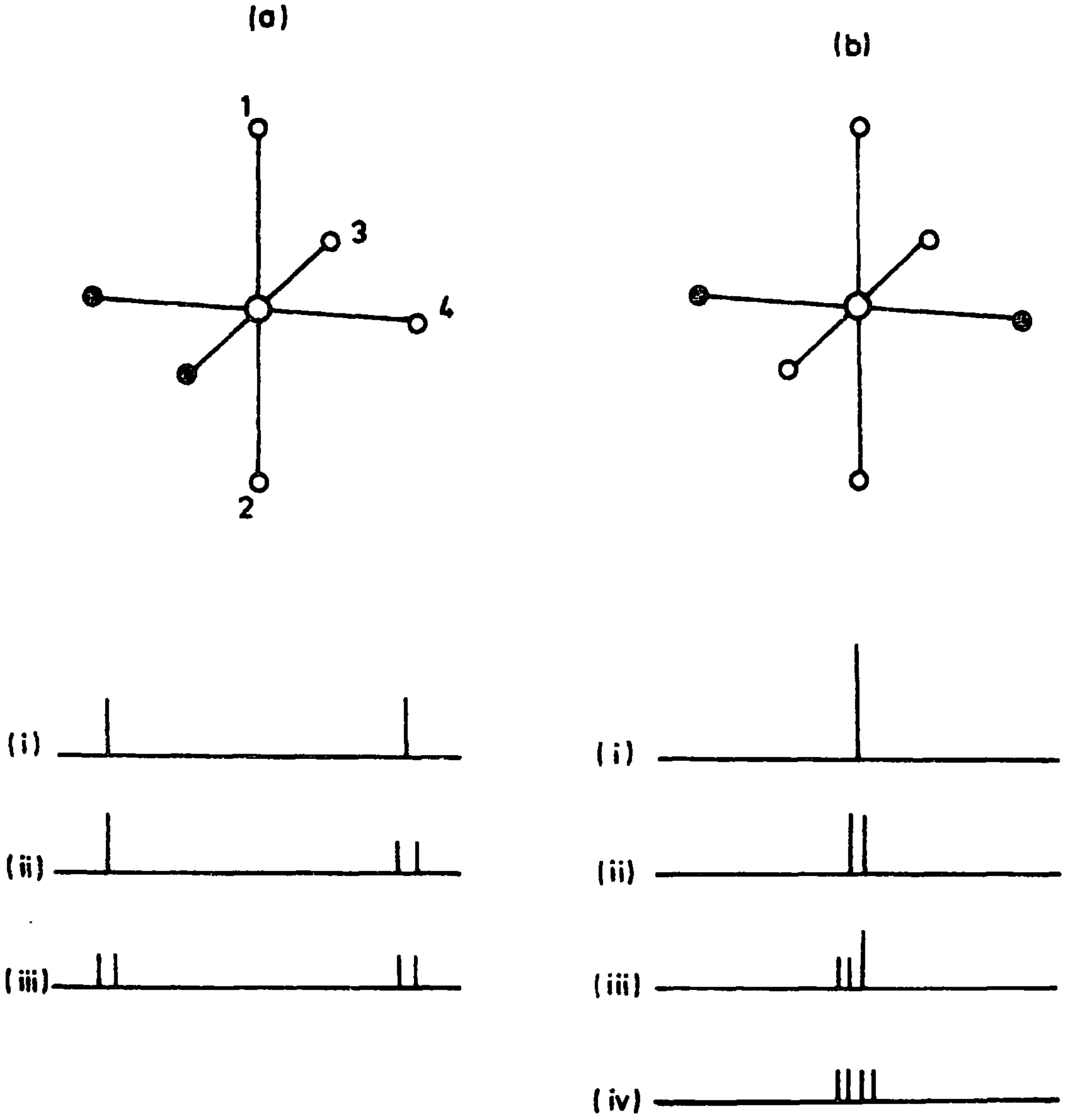
4.3 Results and Discussion

4.3.1 Stereochemistry of the Adducts

An approximate molecular orbital treatment applied to the effect of donor molecules that are *cis* or *trans* on the electric field gradient at a nucleus in a pseudo octahedral complex[19,20] shows that the average shifts in NQR frequencies for the *cis* and *trans* isomers will not be the same and in a *cis* adduct the NQR frequency will be different for the axial and equatorial chlorine nuclei.

This conclusion also follows from an empirical consideration of the *cis* and *trans* structures shown in Figure 4.1. At least two resonances (Figure 4.1.a.i) are expected from the *cis* adduct arising from the two distinct types of chlorine atom (axial and equatorial) though either of these resonances (Figure 4.1.a.ii) or both of them (Figure 4.1.a.iii) may be further split if the chemically equivalent nuclei occupy different lattice sites. In contrast the spectrum of the *trans* adducts may consist of a single resonance (Figure 4.1.b.i) since all four chlorine atoms occupy chemically equivalent positions. However secondary, crystallographic inequivalence may generate a total of two, three or

Figure 4.1
Isomers of $SnCl_4L_2$ and possible
^{35}Cl N.Q.R. Spectra



four resonances (Figure l.b.i-iv). The crystallographic splittings are always small relative to the chemical shifts and are considered unlikely to exceed 2%[25] - 5%[26] of the observed absorption frequency.

A typical NQR spectrum of $SnCl_4$.2ACN (as recorded) is shown in Figure 4.2. Details of all the spectra recorded are given in Table 4.2. They are also presented graphically in Figure 4.3 from a single temperature (77K). The spectra recorded at a single temperature do not fall obviously into any one category of those discussed above. For this reason the temperature dependence of the absorptions were determined by recording them at 77K (liquid nitrogen), 195K (dry ice) and 300K (Room Temperature).

Figures 4.4-7 illustrate the temperature dependence of the spectra for $SnCl_4$.2RCN (R = Me, CH_2:CH, Bu^t,Ph). Chemically equivalent nuclei are expected to show a similar temperature-absorption frequency coefficient ($d\nu/dT$). In each of the Figures 4.5-7 there are indeed two distinct types of temperature dependence in each case, with pairs of lines having closely related temperature coefficients (Table 4.2) corresponding to the axial and equatorial chlorine sites in a *cis* adduct. For L = ACN this situation could only be elucidated by recording spectra at more temperatures than normal due to the unusual crossover of two of the absorptions. The situation is less clear for $SnCl_4$.2MeCN but similar temperature dependence is shown by at least one pair of lines and the overall spread of frequencies (0.43MHz) is too great to be attributable to a solid state splitting of chemically equivalent nuclei. Therefore a *cis* configuration is again indicated.

Figure 4.2

^{35}Cl N.Q.R. of $SnCl_4.2ACN$ at 77K

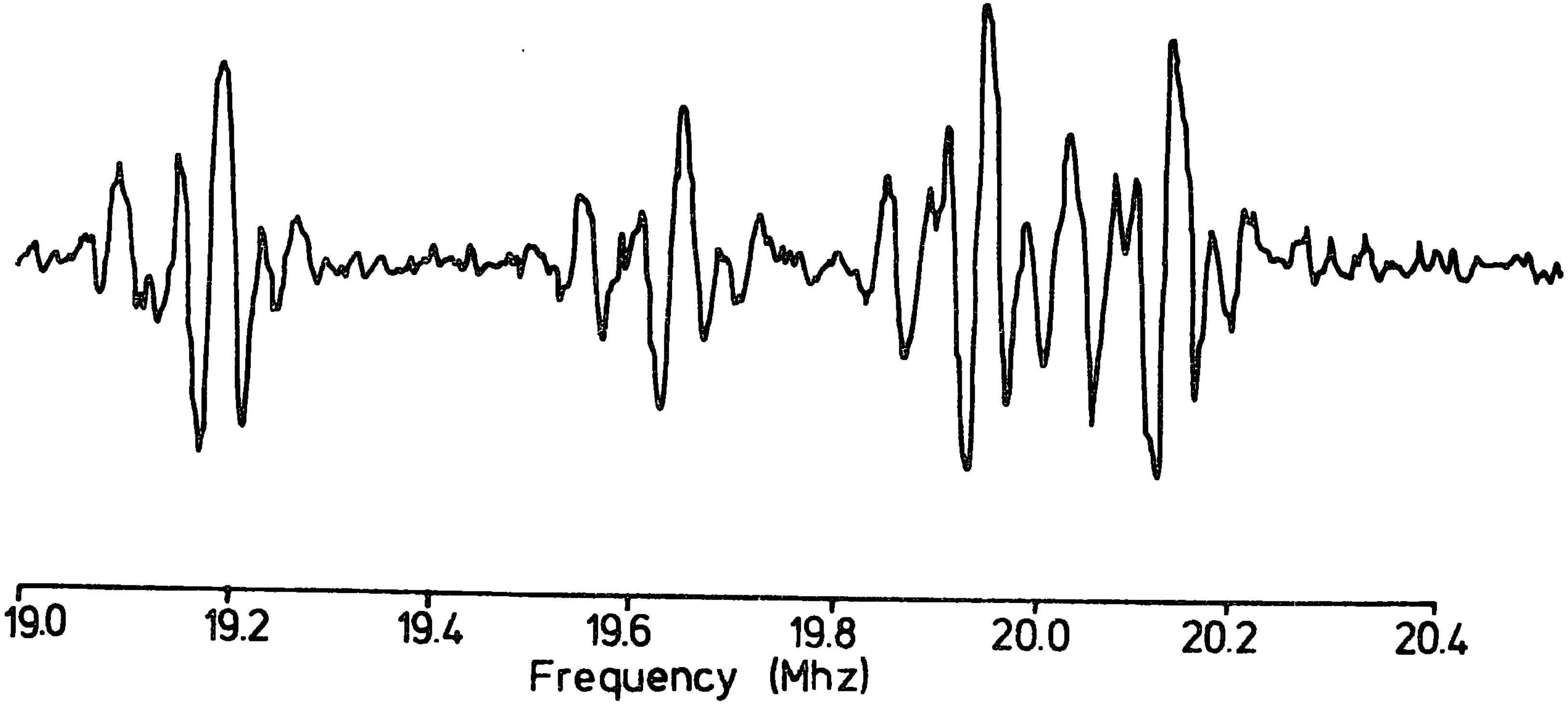


TABLE 4.2 ^{35}Cl N.Q.R. Frequencies at Various Temperatures of $SnCl_4$ Adducts

Compound	^{35}Cl N.Q.R. Frequency (MHz)$^{\emptyset}$			$(\frac{d\nu}{dT})_{av}$ (HzK^{-1})
	77K	195K	300K	
$SnCl_4$†	23.720			
	24.140			
	24.226			
	24.296			
$SnCl_4$.2MeCN	19.192	19.225	19.175	-76
	19.580	19.545	19.475	-426
	19.825	19.750	19.725	-448
	20.625	20.514	20.433	-861
$SnCl_4$.2ACN	19.19	19.13	18.96	-1013
	19.64	19.66	19.56	-359
	19.94	19.80	20.65	-1300
	20.13	20.15	20.11	-90
$SnCl_4$.2Bu^{t}CN	19.390	19.180	18.800	-2650
	19.535	19.278	18.925	-2740
	19.650	19.558	19.406	-1090
	20.285	20.217	20.025	-1170
$SnCl_4$.2PhCN	19.753	19.61	19.33	-1897
		19.85	19.85	+435
$SnCl_4$.2$CH_2(CN)_2$	19.40(2)	19.35(2)	19.35(2)	-224
	20.10(1)	20.13(1)	20.19(1)	+403
	21.57(1)	21.57(1)	21.58(1)	+44

TABLE 4.2 (continued)

$SnCl_4.2(1,2C_6H_4(CN)_2)$	19.08(2)	-	-	-
	22.09(1)	-	-	-
	22.22(1)	-	-	-
$SnCl_4.2Me_2SO$	16.92	16.86	16.7*	-942
	17.17	16.96	16.8*	-1704
	17.98	17.86	17.7*	-1166
	18.74	18.52	18.4*	-1570
$SnCl_4.2THT$	17.42	17.33	-	-763
	17.88	17.75	-	-1102
$(Ph_2CNH_2)_2SNCl_6$	16.19(1)	-	16.11(1)	-381
	17.70(2)	-	16.35(1)	-6053
	-	-	18.14(1)	+1973

∅ Peaks are of equal intensity unless relative intensities are given in parentheses

† Ref. 21

* No resonances were observed for $SnCl_4.2Me_2SO$ at 300K. The frequencies listed are estimated values obtained by extrapolation from the spectra at 77K and 195K assuming a linear variation of frequency with temperature.

Figure 4.3

^{35}Cl N.Q.R. Spectra of SnCl$_4$L$_2$ at 77K.

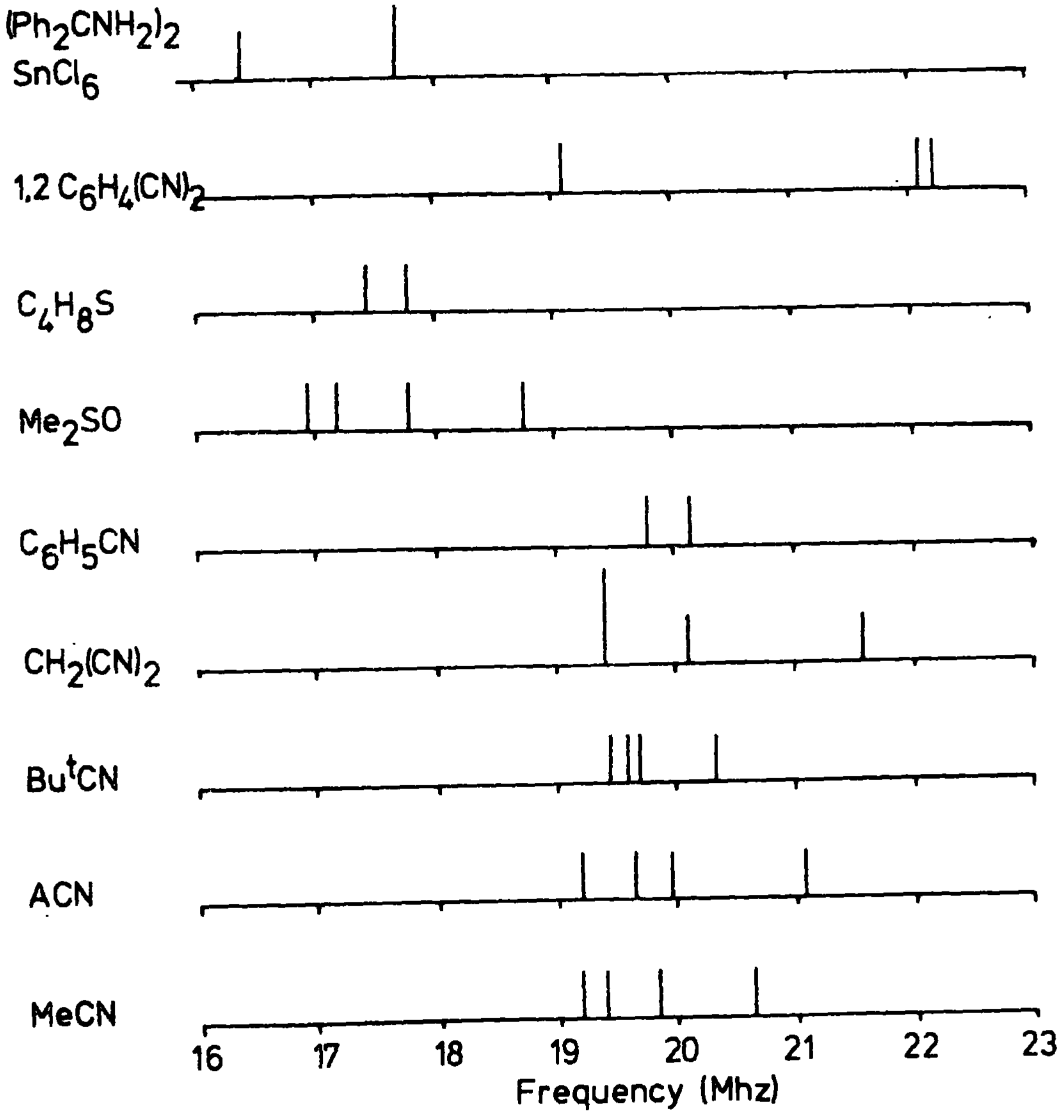


Figure 4.4 ^{35}Cl NQR Temperature Dependence

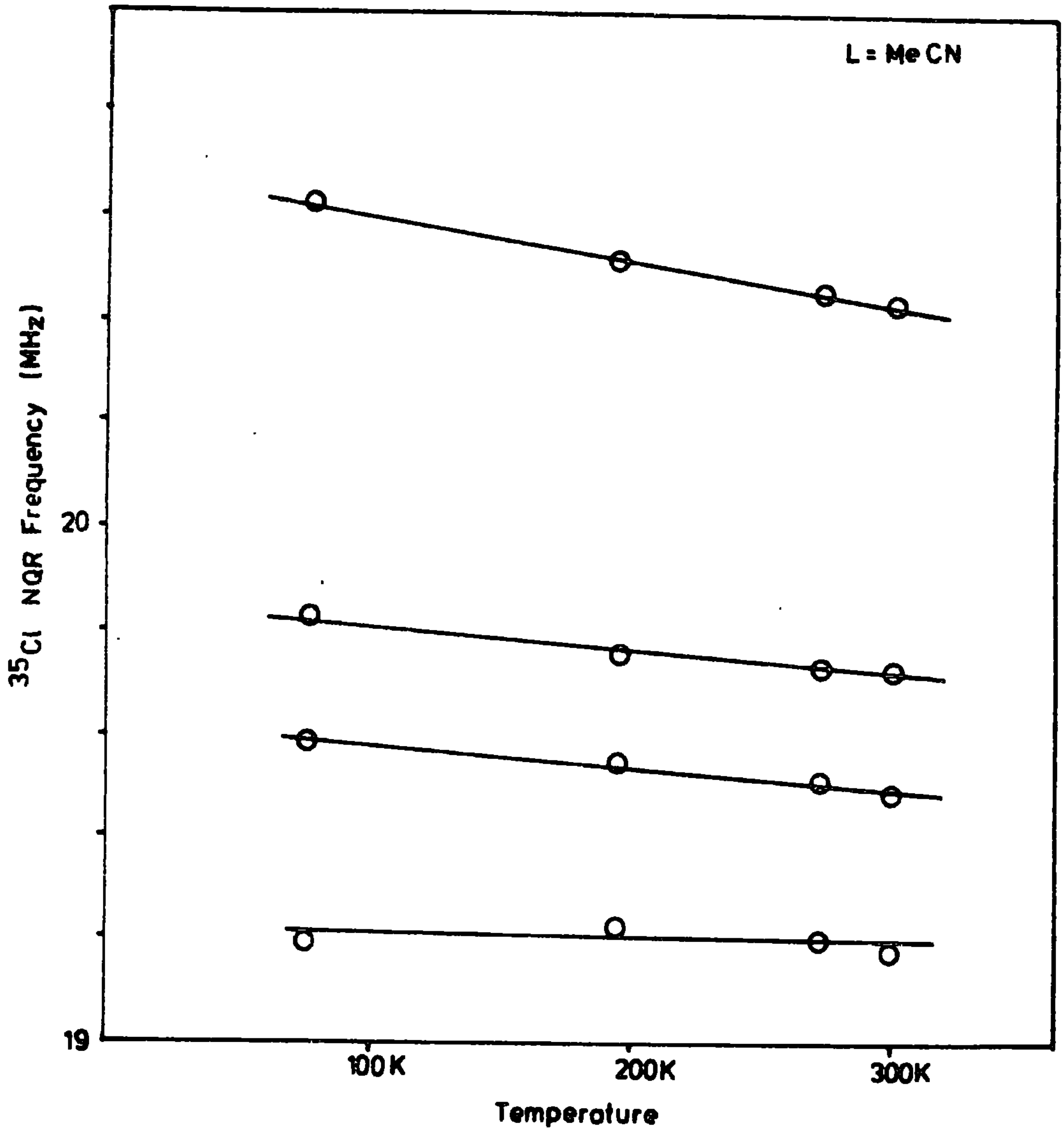


Figure 4.5 ^{35}Cl NQR Temperature Dependence

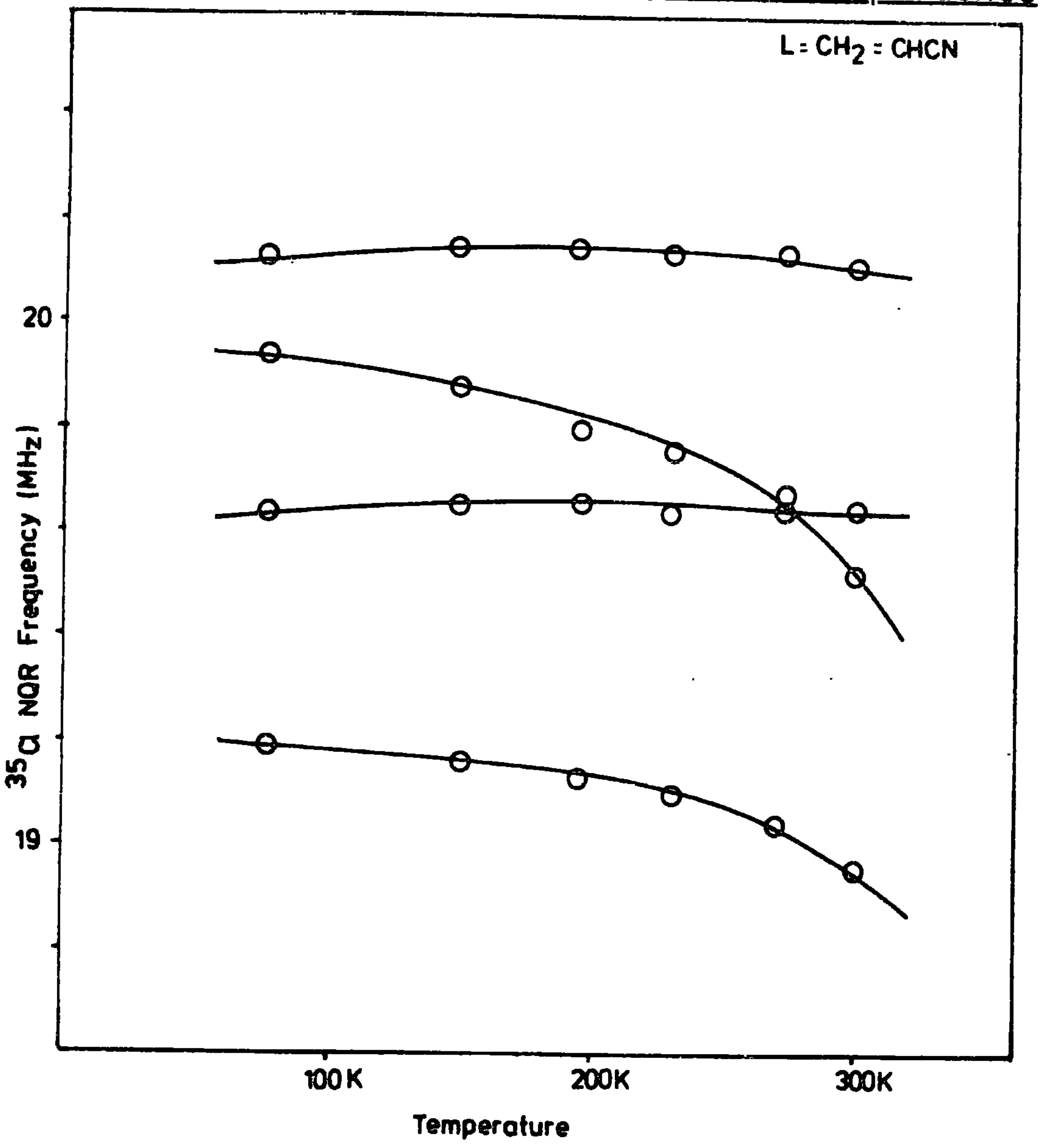


Figure 4.6 ^{35}Cl NQR Temperature Dependence

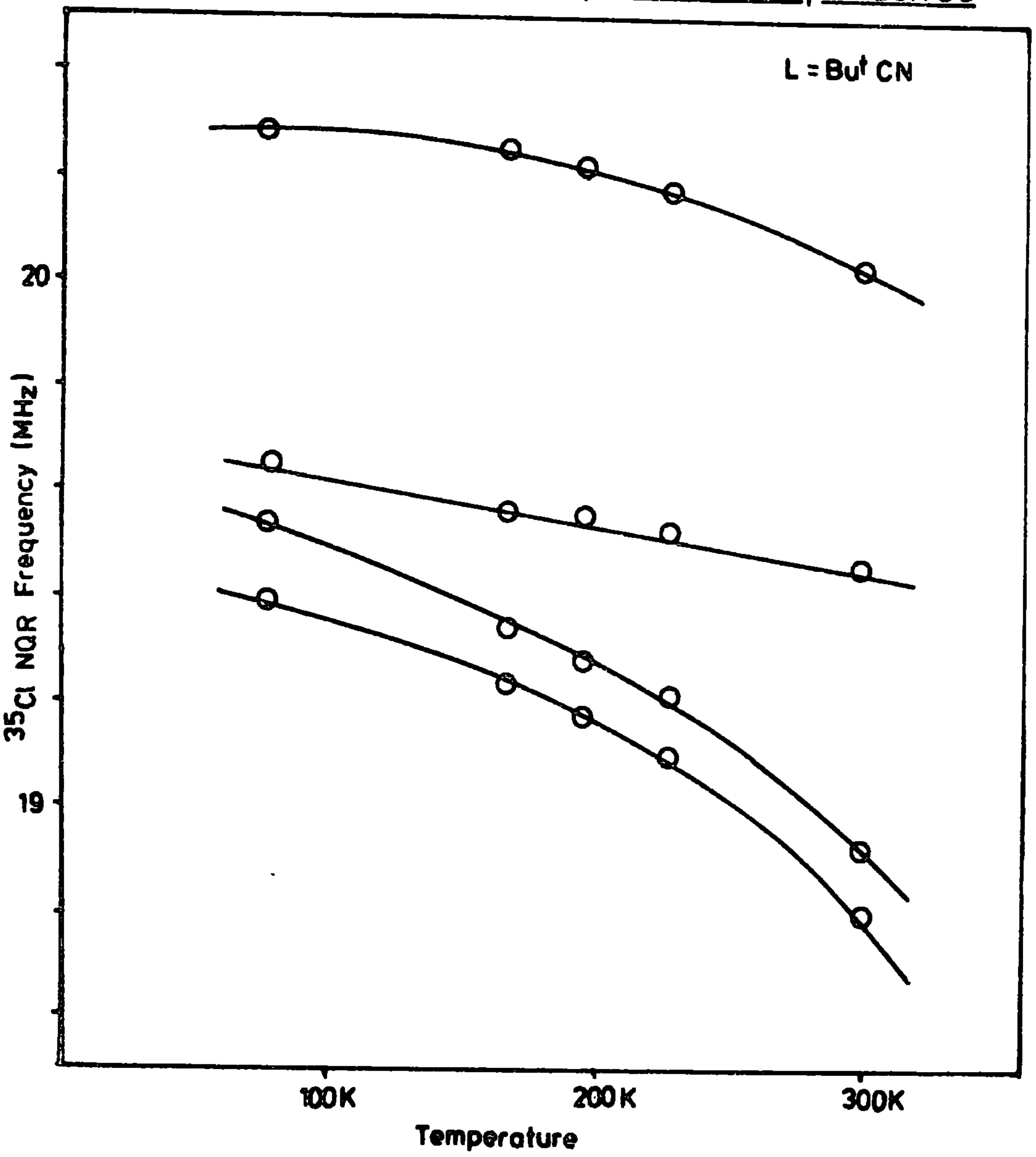
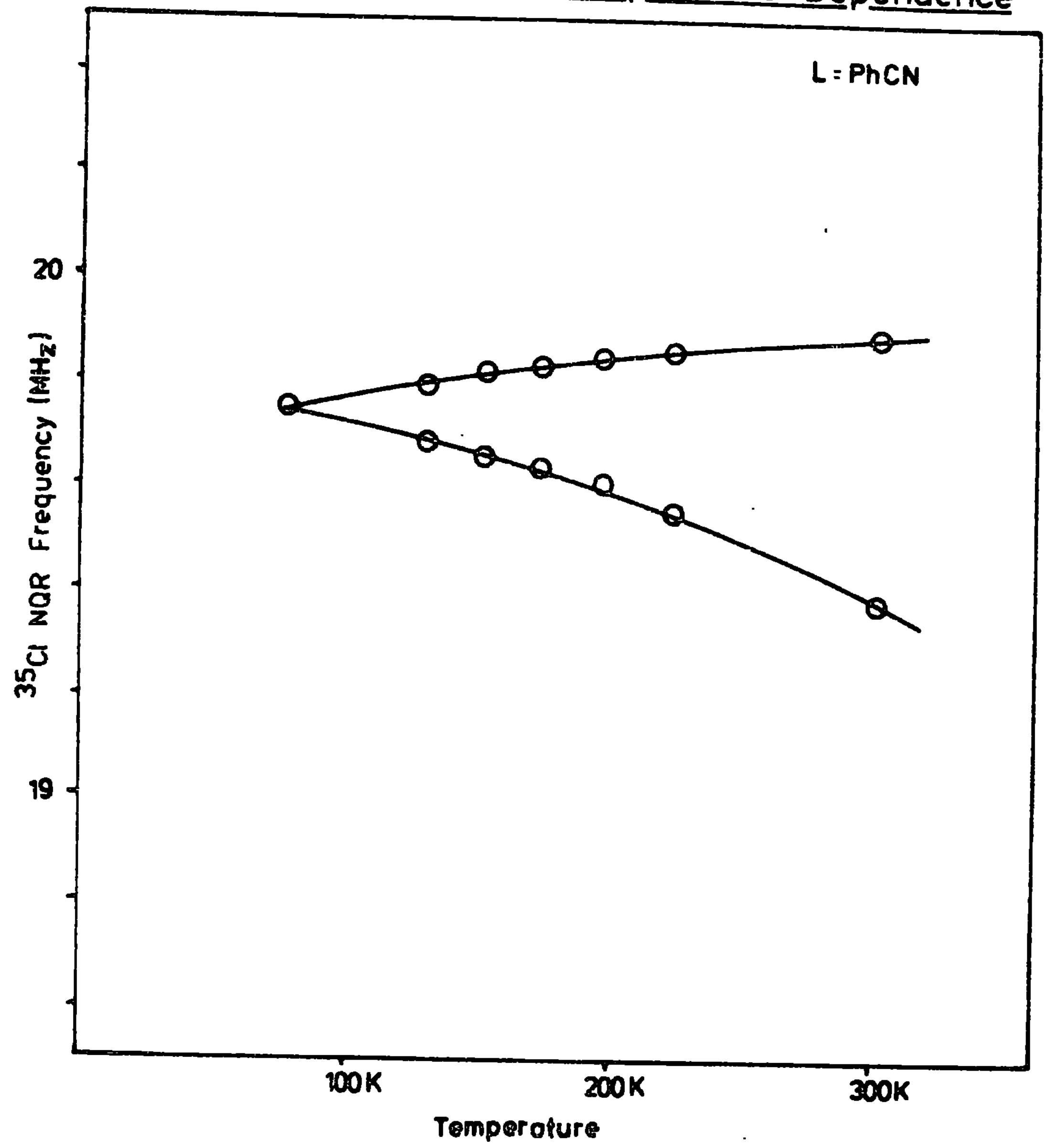


Figure 4.7 ^{35}Cl NQR Temperature Dependence



Unfortunately our samples of the adducts with $L = Me_2SO$, $CH_2(CN)_2$, $o NCC_6H_4CN$ did not give satisfactory spectra throughout the range. This situation is not uncommon as line intensities are usually (but not always) greater at lower temperatures because there is a more favourable Boltzmann distribution of energy level populations and there is less broadening from molecular librations at low temperatures. However the appearance of widely spaced lines of relative intensity 1:1:1:1 ($L = Me_2SO$) and 2:1:1 ($L = CH_2(CN)_2$, $o NCC_6H_4CN$) at 77K suggests that these structures also have a *cis* configuration. Indeed the adducts $SnCl_4.2MeCN$ and $SnCl_4.2Me_2SO$ are known to have *cis* structures.[4,5] It appears that nitriles generally adopt a *cis* configuration. This is probably because a nitrile is effectively a pointed ligand, the donor atom projecting some 460pm from the alkyl or aryl substituent. Hence crowding of one ligand by another in a *cis* adduct is not important even in the case of Bu^tCN. The same is probably true of the sulphoxide ligand.

The tetrahydrothiophene adduct, $SnCl_4.2THT$ gives a ^{35}Cl NQR spectrum (Figure 4.3) containing two closely spaced lines with a similar temperature dependence thus resembling ether adducts $SnCl_4.2R_2O$[14] and confirming the *trans* structure that had been inferred from a vibrational spectroscopic study[13] supported by X-ray powder photographs and dielectric constant data.

Other workers[15] have reported that adding THT to a pentane solution of $SnCl_4$ affords the *cis* adduct. However we found no evidence for this. The NQR spectra of the two $SnCl_4.2THT$ samples and the temperature dependences are identical and consistent with a *trans* structure.

4.3.2 Infra-Red Spectra of $SnCl_4.2L$

Although the ^{35}Cl NQR data listed in Table 4.2 provide a useful insight into the stereochemistry of these adducts and so illustrate the value of nqr for structure determination, the limitations of the method were apparent when we attempted to record the spectra of 6 further adducts, $SnCl_4.NC(CH_2)_nCN$ (n = 2,3[8],4), $SnCl_4.2L$ (L = $4MeC_6H_4CH_2CN$[14], $2MeC_6H_4CH_2CN$[4], Py[9]). No resonances could be detected at any temperature for these compounds. In view of this we felt it worthwhile to record the infra-red spectra off all the compounds prepared and attempt to analyse the far infra-red region (250-450 cm^{-1}) where metal ligand vibrations are expected to occur. The far infra-red spectra are tabulated in Table 4.3.

Theoretically 15 normal vibrations (3x7-6) are expected for the $SnCl_4.2L$ molecule if the ligand L is assumed to be a point mass. The vibrations for a *trans* adduct (D_{4h} symmetry) are given by equation

$$\Gamma = 2A_{1g} + B_{1g} + B_{2g} + E_g + 2A_{2u} + B_{2u} + 3E_u$$

Only the A_{2u} (Sn-L) and E_u (Sn-Cl) bands are infra-red active.

In the *cis* case (C_{2v}) the vibrational modes are given by equation

$$\Gamma_{vib} = 6A_1 + 2A_2 + 3B_1 + AB_2$$

The A_1, B_1 and B_2 vibrations are infra-red active of which four are Sn-Cl vibrations ($2A_1 + B_1 + B_2$) and two are Sn-L modes ($A_1 + B_2$).

Hence in the absence of crystallographic differences of ligands one expects generally more bands in the far infra-red region in the *cis* adduct than in the *trans* case.

TABLE 4.3 Infra-Red Absorptions between 250 cm^{-1} and 450 cm^{-1} in $SnCl_4$ adducts

Ligand	Stoichiometry	Absorption Maxima
MeCN	2	308s, 340s,br, 365s,br, 390m, 405m
ACN	2	308s, 340s,br, 360s, 402s
Bu^tCN	2	268m, 308m, 340s,br, 360s,br, 405s
PhCN	2	255sh, 308m, 345s, 360s, 400w
$2,MeC_6H_4CH_2CN$	2	255w, 305s, 330s, 355s, 382m, 393m, 405sh, 435sh
$4,MeC_6H_4CH_2CN$	2	290m, 303m, 330s, 337s, 372s, 390sh, 420m
$CH_2(CN)_2$	2	255w, 315s, 340s, 375s, 405m
$NC(CH_2)_2CN$	1	260m, 320s, 345s, 378s, 400sh
$NC(CH_2)_3CN$	1	250m, 280w, 305m, 315m, 340s, 380s, 400sh
$NC(CH_2)_4CN$	1	258m, 298m, 315m, 340s, 368s, 390w
Me_2SO	2	250w, 272m, 305s, 338s
THT	2	268w, 305sh, 323s
C_5H_5N	2	310sh, 330s, 440m

This is found to be the case on consideration of the absorptions in the region 250 cm^{-1} - 450 cm^{-1}. It is evident however that a strict correlation with the group theory predictions does not occur. In the *cis* adducts (L = RCN,Me_2SO) not all the expected absorptions are observed due to band coalescence. In the *trans* (L = THT,py) splitting must occur to explain the observation of 3 bands instead of the predicted 2.

4.3.3 Lewis Base Strengths

For tin IV chloride adducts $SnCl_4.2L$ the drop in ^{35}Cl NQR frequency (relative to uncoordinated $SnCl_4$) on complex formation is expected to reflect the donor properties of the ligand L.[27-29] This arises because a strong Lewis base will transfer more electron density to the chlorine atoms of the $SnCl_4$ making them more ionic and so reducing their nqr frequencies. On this baais the averages of the nqr frequencies in Table 4.2 lead to the following sequence of Lewis base strengths:

1,2 $C_6H_4(CN)_2$ < $CH_2(CN)_2$ < $POCl_3$ < MeCN < PhCN ⩽ CH_2:CHCN $\sim Bu^t$ < Me_2SO

4.3.4 Sn-Cl Bond Length -^{35}Cl NQR frequency correlation

Correlations between the ^{35}Cl NQR frequency and M-Cl bond lengths are to be expected in a simple unperturbed system since the bond length is reflective of the degree of ionicity in the bond and hence the electric field gradient at a nucleus. Correlations have been noted in several systems.[30-33]

Linear relationships between bond length and nqr frequencies have been reported for cyclo phosphazenes[30,31] Figure (4.10), platinium II chloride adducts[32] and tetrachloroiodates[33], and a non-linear but well defined relationship has been noted for a series of mercury II chloride compounds.[34] Our own nqr data together with data from the

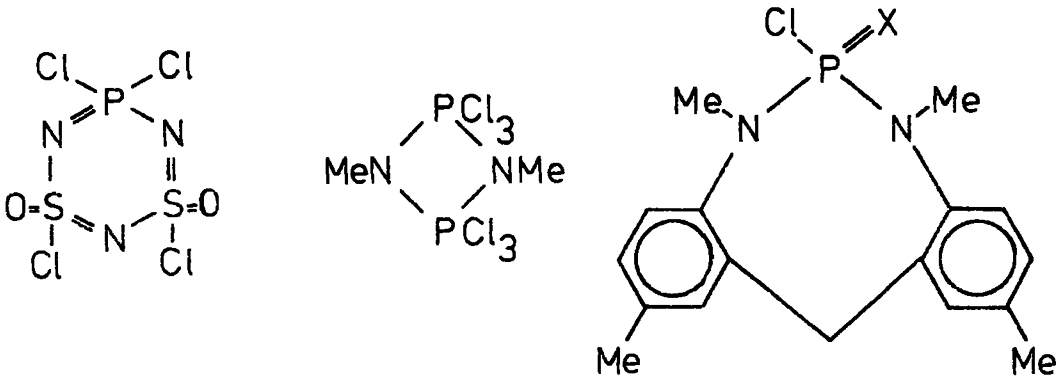


Figure 4.10

literature (Table 4.4) shows that despite the sometimes marked temperature dependence of nqr frequencies, illustrated by Table 4.2, a linear correlation between ^{35}Cl NQR frequencies and Sn-Cl bond lengths exists in the case of tin IV chloride adducts.

The correlation has been investigated with 3 methods of assignment. Firstly the average bond length may be plotted against the average NQR frequency. This gives the plot shown in Figure 4.11.

In order to make better use of the available data it is necessary to assign particular resonances to specific chlorine nuclei. One method of assignment commonly adopted is to assume that the longest bonds in a particular compound have the greatest ionic character and hence the lowest nqr frequency, as is usually the case if there is little or no π bonding contribution to the M-Cl bond. Figure 4.12 shows the data from Table 4.4 plotted on this basis.

TABLE 4.4 Sn-Cl Bondlength vs ^{35}Cl N.Q.R. Correlations

Compound	d(Sn-Cl) (pm)	Ref.	^{35}Cl NQR Frequency (MHz)		
			A	B	C
$SnCl_4.2MeCN$	235.6	5	19.705	19.175	19.175
	235.5			19.485	19.725
	234.1			19.725	19.485
	233.9			20.433	20.433
$SnCl_4.2Me_2SO$	247	4	17.4	16.7	17.7
	244			16.8	16.7
	242			17.7	16.8
	236			18.4	18.4
$SnCl_4.2POCl_3$	236	7,36	19.968	18.873	18.873
	233			19.110	20.945
	231			20.945	19.110
$(4ClC_5H_4NH)^+_2$ $SnCl_6^-$	246.3	26,37	16.60	14.97	
	241.9			17.32	
	241.4			17.52	
$(Ph_2CNH_2{}^+)_2$ $SnCl_6^-$	245.6		16.86	16.10	
	242.6			16.35	
	241.3			18.14	
$(Me_4N)_2SnCl_6$	240.2	38	16.663		
K_2SnCl_6	241.1	38	15.064		
Rb_2SnCl_6	242.3	38	15.60		
Cs_2SnCl_6	242.3	38	16.05		
$(NH_4)_2SnCl_6$	242.1	38	15.475		

Figure 4.11. ^{35}Cl N.Q.R. vs Sn-Cl Bondlength.Method A

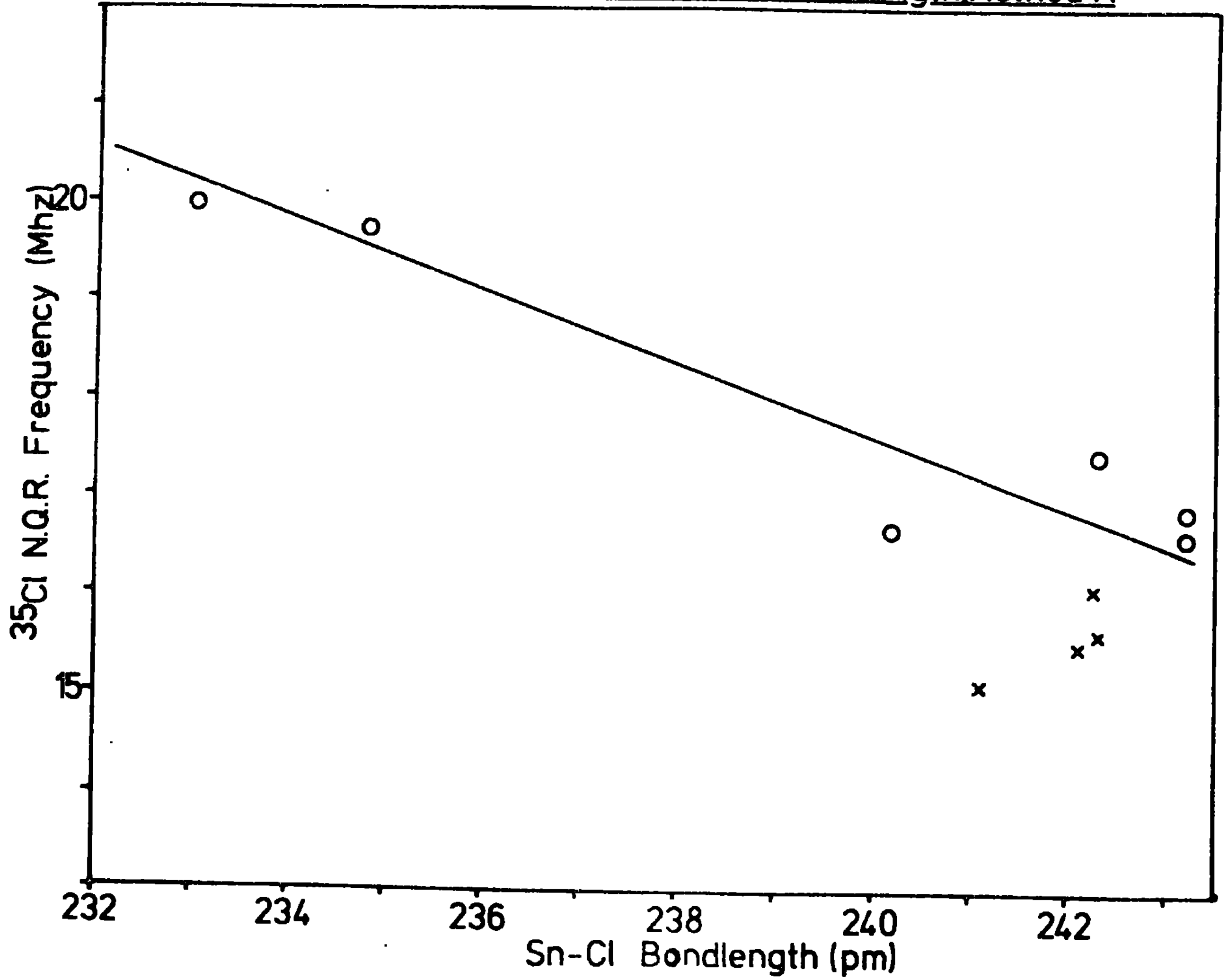
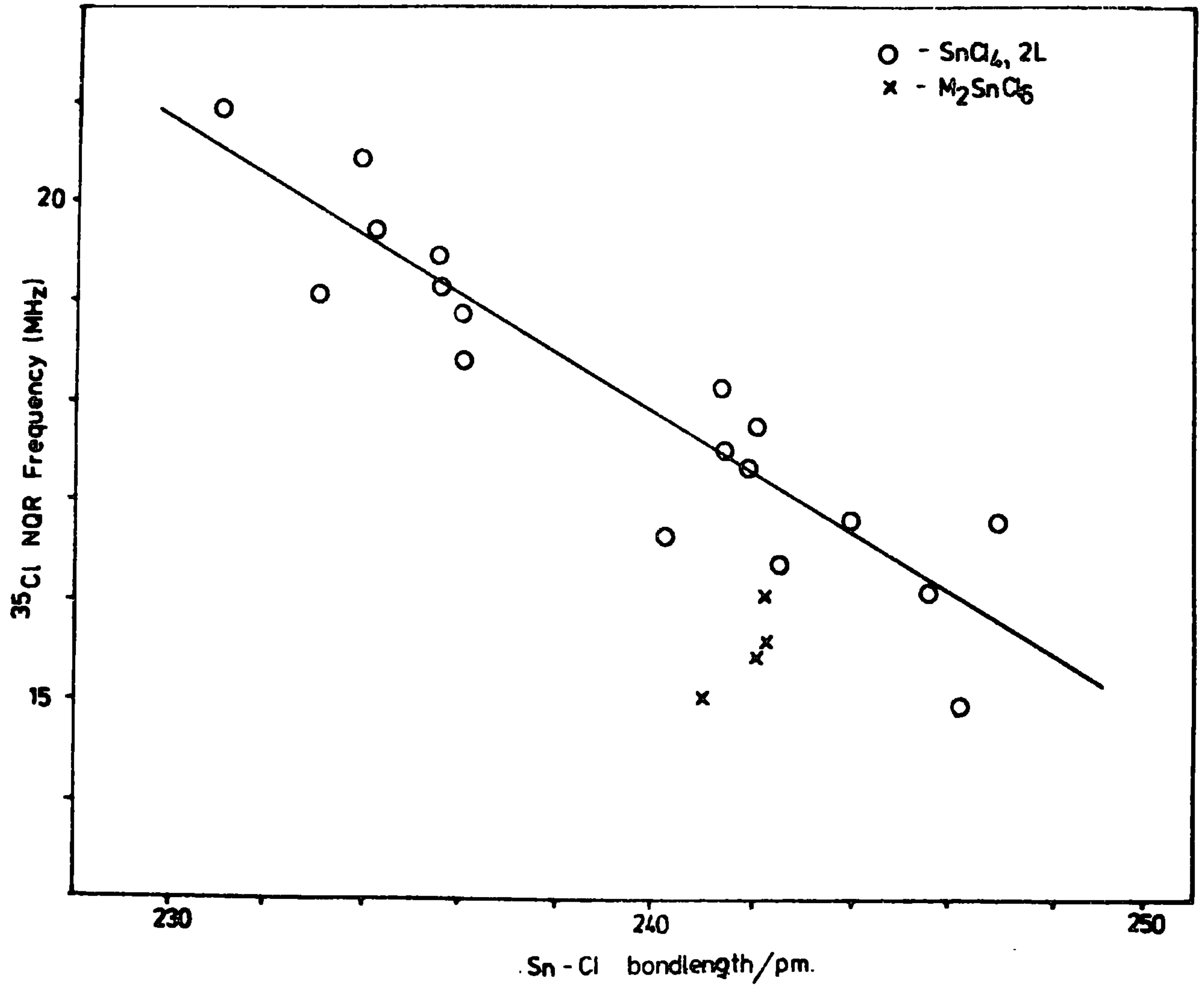


Figure 4.12. ^{35}Cl N.Q.R. vs SnCl Bondlength.Method B

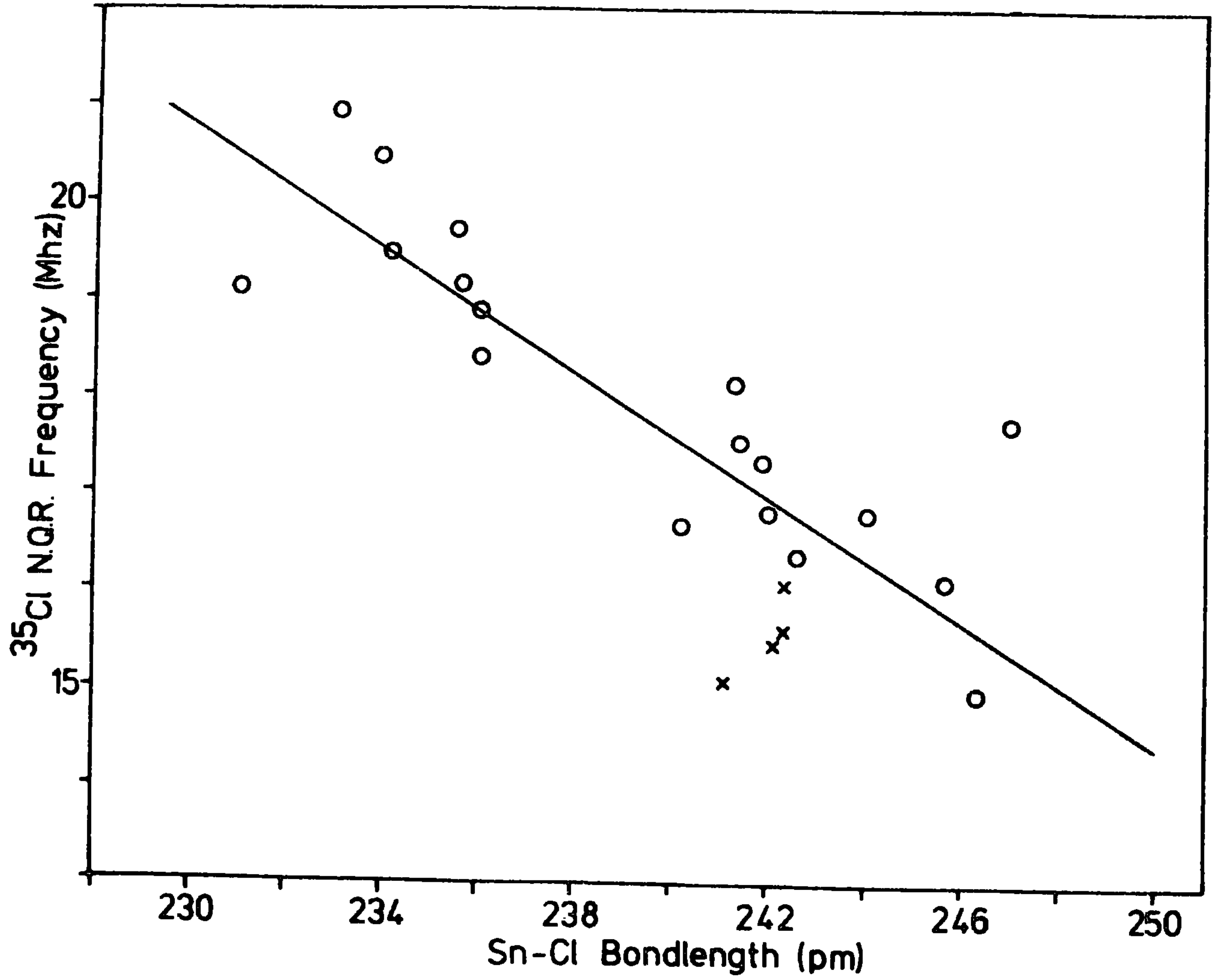


An alternative method of assignment is to use the compound *cis* $SnCl_4.2POCl_3$ as a model and the *trans* effect as proposed by Syrkin[35], to enable this method of assignment to be extended to the other compounds. In the adduct $SnCl_4.2POCl_3$ the axial chlorines have the same Sn-Cl bond length, 233pm[6], whilst the equatorial chlorines are unequivalent (231,236pm). The axial chlorines are therefore assigned to the highest intensity resonance at 20.945MHz, also the highest frequency resonance. This is in agreement with the *trans* effect which simply proposes that a ligand is electronically more sensitive to another ligand in a *trans* position than a *cis*. Therefore since Cl is a poorer donor of electron density than any of the ligands considered here, the axial chlorines will have less electron density donated to them than the equatorial chlorines *trans* to the donor molecules. Thus the axial chlorines will be more covalently bonded and have a higher nqr frequency.

In the other adducts the highest frequency resonances are accordingly assigned to the axial chlorine atoms. The remaining two resonances must then be assigned using the 'longest bond gives rise to the lowest frequency' criterion. Although this method leads to some assignments which differ from those made on the basis of bond lengths the same overall correlation between $\nu(^{35}Cl)$ and d(Sn-Cl) exists as shown in Figure 4.13).

The correlation coefficients for all 3 methods of analysis are given in Table 4.5. The considerable deviation of certain points from the linear relationship shown in Figures 4.12 and 4.13 probably arise from the perturbation of the electric field gradient at certain nuclei by neighbouring

Figure 4.13. ^{35}Cl N.Q.R. vs Sn-Cl Bondlength.Method C



ionic nuclei. In studies of the hexachlorostannates of K^+, Rb^+, Cs^+, NH_4^+ and Me_4N^+, Brill and coworkers[38] conclude that there is no bond length frequency correlation for these salts because of perturbation of the $SnCl_6^{2-}$ anions by the cations. For this reason the data for the potassium, rubidium, caesium and ammonium salts have been omitted from the regression procedure. Table 4.5 shows the effect on r^2 (residual) of their inclusion. However the correlation with the other data improves as the cation becomes softer (i.e. in the sequence $K^+ < Rb^+ < Cs^+ < NH_4^+ < Me_4N^+$) and thus the data for Me_4N^+ are included in the regression.

4.4 Conclusions

The applicability of the empirical relations developed above probably imply that the asymmetry parameter, η, of the electric field gradient around the ^{35}Cl nucleus is either small or does not vary from one complex to another so that the observed nqr frequency is directly related to the nuclear quadrupole coupling constant. Evidence from the study of ^{127}I nqr in SnI_4 and $SnI_4.2S_8$ where the asymmetry parameter can be determined directly indicate that it has a value of less than 0.04.

In view of the broad correlation between $\nu(^{35}Cl)$ and d(Sn-Cl) that has been illustrated we consider that Sn(5d)-Cl(3p) bonding is not significant in these systems, because if it were the shorter bonds would be expected to give rise to lower nqr frequencies, a trend opposite to that observed.

TABLE 4.5 Linear Relationships (y=mx+c) between ^{35}Cl Frequencies (y in MHz) and d(Sn-Cl) bond Lengths (x in pm)

Coefficient	Method of Assignment		
	A	B	C
m	-33.20	-30.73	-29.56
c	97.34	91.58	88.82
$^{+}r^2$	0.90	0.87	0.76
m^*	-40.26	-33.88	-32.92
c^*	113.72	98.86	96.55
r^{2*}	0.73	0.78	0.69

\+ r^2 = correlation coefficient

* regression computed including data for M_2SnCl_6(see text)

A relates average frequency to average bond length for each compound

B relates individual frequencies to individual bond lengths by the method of "longest bond gives lowest frequency"

C relates individual frequencies to individual bond length by the method of "the *trans* effect"

CHAPTER FIVE

The Reaction of Tin Dichloride and Hydrogen Chloride with Nitriles

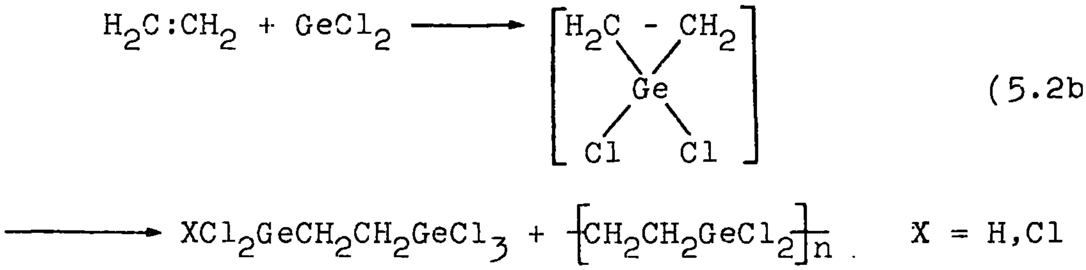
5.1 Introduction

The reaction of hydrogen chloride and tin dichloride has been reported to yield solvated trichlorostannane, $HSnCl_3.nL$(I) (L = solvent).[1-11] Engel[1] first reported the preparation of $HSnCl_3.3H_2O$ by cooling an aqueous solution of tin dichloride saturated with hydrogen chloride. Conductivity studies[2] indicated the presence of species such as $SnCl_3^-$ and $SnCl_4^{2-}$. The formation constants for equation 5.1 have also been determined,[3] based on

$$Sn^{2+} + nCl^- \rightleftharpoons SnCl_n^{2-n} \qquad n = 1\text{-}4 \qquad (5.1)$$

emf data from concentration cells. Russian workers[4-6] have studied the structure and properties of trihalogermane etherates, such as $HGeCl_3(Et_2O)_2$ which behave as pseudo carbenes, equation 5.2a, towards alkenes and alkynes, equation 5.2b.

$$HGeCl_3.nEt_2O \rightleftharpoons (GeCl_2) + Et_2{}^+OH + Cl^- \qquad (5.2a)$$



(5.2b)

However they state that trichlorostanne etherate does not form organotin compounds with unsaturated hydrocarbons.

In contrast, a patent application[7] suggests that (I) does react with α alkenes to give the corresponding alkanes, equation 5.3.

$$HSnCl_3 + H_2C{:}CHR \longrightarrow Cl_3SnCH_2CH_2R \qquad R = \text{alkyl, H} \qquad (5.3)$$

More recently $SnCl_2$ and HCl in ether have been found to react with α, β unsaturated carbonyl compounds such as acrylic esters and amides to give β substituted alkyl tin trichlorides[8,9] (e.g. 5.4) in high yields.

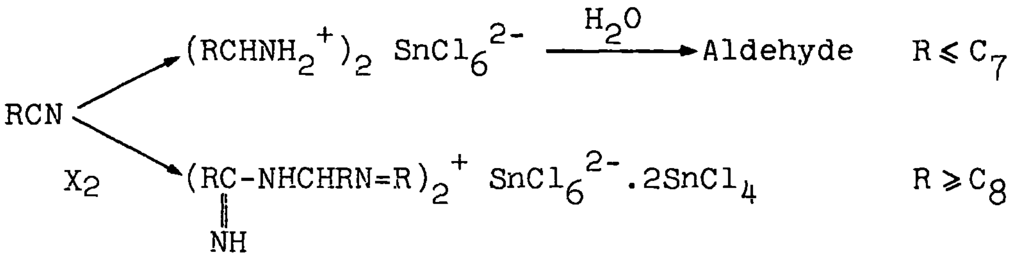
$$HCl + SnCl_2 + CH_2 = CH\ COOMe \longrightarrow Cl_3SnCH_2CH_2\ COOMe \quad (5.4)$$

The same workers also describe the preparation of substituted dialkyl tin dichlorides[9,10,11] from metallic tin and hydrogen chloride (e.g. equation 5.5) postulating the formation of (H_2SnCl_2) or (HSnCl) as reactive intermediates. This synthesis is also the subject of two patents by independent workers.[12,13]

$$\begin{aligned} 3Sn + 5HCl + 3CH_2 = CH\ COOMe \longrightarrow\ & Cl_3SnCH_2CH_2COOMe \\ & + Cl_2Sn(CH_2CH_2COOMe)_2 + H_2 \end{aligned} \quad (5.5)$$

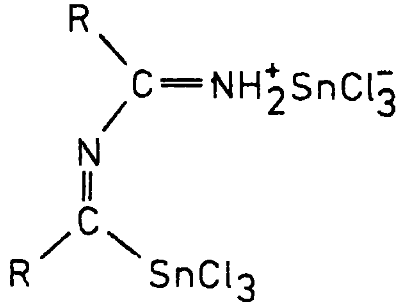
Independent of the work on the reaction between HCl, $SnCl_2$ and olefins certain nitriles undergo reduction by $SnCl_2$ and HCl in ether by the Stephen Reaction to give aldehydes on hydrolysis.[14] The literature regarding the scope of the reaction and its mechanism is inconsistent. Stephen's original work[14] claims virtually quantitative conversion to aldehyde but this has never been repeated.[15] Common by-products after hydrolysis are primary amides and trimers, NN´alkylidene bisamides, (RC:ONHCHRNHC:OR)[16]. Dimers have also been observed[17] but subsequent workers[18] were unable to repeat this.

Russian work[14] has shown that the reaction may be complicated by the cleavage of ether by HCl and subsequent ethanolysis of products. The most recent study[20,21](1963), in attempting to explain previous results from analytical information on intermediates has shown that the yield of aldehyde decreases and the yield of amide and trimer increases as the alkyl chain length increases. The current knowledge may be summarized in equation 5.6.



$$\mathrm{RCN}\ \begin{array}{l} \nearrow (\mathrm{RCHNH_2^+})_2\ \mathrm{SnCl_6^{2-}} \xrightarrow{\mathrm{H_2O}} \mathrm{Aldehyde} \qquad R \leqslant C_7 \\ \underset{X_2}{\searrow} (\mathrm{R\underset{\underset{NH}{\|}}{C}{-}NHCHRN{=}R})_2^+\ \mathrm{SnCl_6^{2-}.2SnCl_4} \qquad R \geqslant C_8 \end{array} \qquad (5.6)$$

In view of the reactivity of HCl and $SnCl_2$ towards alkenes and nitriles we were interested in exploring how this system would react with nitriles and especially ACN since this has two sites for possible addition. Whilst we did not set out to clarify the mechanism of the Stephen reaction, but rather to study anhydrous reactions of nitriles, our results nevertheless strongly suggest that the currently accepted mechanism of the Stephen's reaction is in need of reappraisal. The major products from the reaction of nitriles other than ACN were dimers with an amidinium structure , Figure 5.1, whereas acrylonitrile reacts by addition of H-Sn across the C=C double bond.



R=Me(III),Et(IV),Bu (V),Ph(VI),

Figure 5.1

5.2 Experimental

All compounds were regarded as air and moisture sensitive and were therefore handled exclusively under dry nitrogen or in a vacuum line. Hydrogen chloride was either used direct from a cylinder (BOC) or dried by using gas evaporating from liquid hydrogen chloride. Anhydrous $SnCl_2$ (BDH) was used without purification since the infra-red spectrum showed it to be water free. All other reagents and solvents were dried by standard methods (see Appendix B).

5.2.i The reaction of acetonitrile with HCl and $SnCl_2$

Tin dichloride (2.89g) was added to 20ml of dry acetonitrile. Hydrogen chloride was passed through the cooled mixture and the $SnCl_2$ was taken into solution in 40 minutes. Hydrogen chloride continued to be passed for 6 hours until a white solid was precipitated. The precipitate was collected on a filter and dried in a steam of dry nitrogen and analysed. On standing overnight the solid turned pale brown.

The solid was found to be *N* (methyl(trichlorostannyl) methylene) acet amidinium trichlorostannate II (Structure III, Figure 5.1) M.P.: 92°C (dec.).

Analyses: see Table 5.1.

Infra-red (cm^{-1}) (Nujol mull): 3340s,br, 3180s,br, 1675s,br, 1550s, 1480s, 1420s, 1388s, 1370m, 1350s, 1300m, 1260m, 1230w, 1140m, 1115s, 1040m, 1028m, 990s, 922m, 792m, 750s, 680s, 525s.

5.2.ii The reaction of propionitrile with $SnCl_2$ and hydrogenchloride

Tin II chloride (3.17g) was added to 10ml of dry propionitrile and then saturated with hydrogen chloride for 12 hours at 0°C. The $SnCl_2$ dissolved during 3 hours to give a straw yellow solution. After 7 days standing at 4°C the solution yielded a fine yellow precipitate which was collected on a filter, washed with propionitrile and pumped dry. The yellow solid, *N*(ethyl,trichlorostannyl methylene) propionamidinium trichlorostannate II (Structure IV, Figure 5.1), was of a waxy consistency M.Pt. 84°C (decomp.)

Analyses: see Table 5.1

Infra-red (cm^{-1}) (Nujol mull): 3510sh, 3320s, 3220s, 1678s, 1648s, 1612m, 1570m, 1480m, 1455m, 1405s, 1390s, 1360s, 1308m, 1245w, 1175w, 1150m, 1125m, 1100m, 1070sh, 1010sh, 1000m, 875w, 835m, 800m.

5.2.iii The Reaction of 2,2,dimethyl propionitrile with tin dichloride and hydrogen chloride

The reaction scheme followed was identical to 5.2.ii. A pale brown solid, *N*(2,2,dimethyl propyl, trichlorostannyl methylene) 2,2,dimethyl propionamidium trichlorostannate II, (Structure V, Figure 5.1) was isolated on filtration, M.Pt.185°C (dec.).

Analyses: see Table 5.1

Infra-Red (cm^{-1}) (Nujol mull): 3320s,br, 3220s, 3180s,br, 1690s, 1540m, 1480m, 1400s, 1118m, 1080m, 1040w, 1025w, 870s, 728w.

5.2.iv The reaction of benzonitrile with tin dichloride and hydrogen chloride

The reaction scheme followed was identical to section 5.2.ii. A white powder, *N*(phenyl,trichlorostannyl methylene) benzamidinium trichlorostannate II (Structure VI, Figure 5.1), was isolated on filtration, M.Pt. 180 (dec.).

Analyses: see Table 5.1.

Infra-red (cm^{-1}) (Nujol mull): 3310s,br, 3160s,br, 2215w, 1720s,br, 1660s,br, 1600s, 1580w, 1545m,br, 1460sh, 1450s, 1445sh, 1330m, 1315m, 1220s, 1185m, 1162w, 1055w, 845sh, 838s, 790s, 780s, 775w, 710w, 700w, 685w, 588w, 550w, 450m, 435w.

5.2.v The Reaction of acrylonitrile with hydrogen chloride and tin dichloride

Anhydrous hydrogen chloride was passed through a slurry of 25g. of $SnCl_2$ in 150ml of dry ether at 0°C. After 1hr. the $SnCl_2$ had dissolved completely. The HCl flow was terminated and the solution allowed to warm to room temperature. A pale yellow oil (50ml) separated on standing. The supernatant ether was syringed off and 40ml of dry ACN was added. The ACN was immediately miscible with oil and was stirred at room temperature for 48 hours.

All volatile components were then pumped off at 0.1mm Hg and the remaining 25ml of straw yellow liquid was distilled *in vacuo* to remove β chloropropinoitrile (6ml collected at 40°C at 1mm Hg). Further heating indicated that a second fraction (B.pt. 130°C at 5mm Hg) was present but this could not be isolated since it was a solid at room temperature and was blocking the still head and condenser.

A solvent extraction method was therefore used.

TABLE 5.1 Analyses for Compounds $R(SnCl_3)C{=}NC(R){:}NH_2^+SnCl_3^-$

Compound	C	H	N	Cl	Sn*	Sn(II)
III,R = Me	9.2(9.0)	2.3(1.9)	5.3(5.2)	39.7(39.7)	40.1)44.2)	21.4(22.1)
IV, R = Et	12.6(12.8)	2.6(2.2)	4.9(5.0)	39.4(38.9)	35.3(42.2)	20.9(21.1)
V, R = Bu^t	19.7(19.4)	3.8(3.2)	4.5(4.5)	35.6(34.4)	27.7(38.5)	Insoluble*
VI, R = Ph	23.6(25.5)	1.7(1.8)	4.3(4.3)	32.7(32.4)	32.6(36.0)	17.9(18.0)
$NCCH_2CH_2SnCl_3$	12.4(12.4)	1.6(1.4)	5.0(5.0)	38.4(38.1)	Not Done	

* See Appendix A for Details

The distillation residues were extracted with 100ml of toluene by refluxing for ½ hr. and filtering off the hot liquors.

Reduction of the liquors yield β cyanoethyl tin trichloride (15g) M.Pt. 107-108°C.

Analysis: see Table 5.1

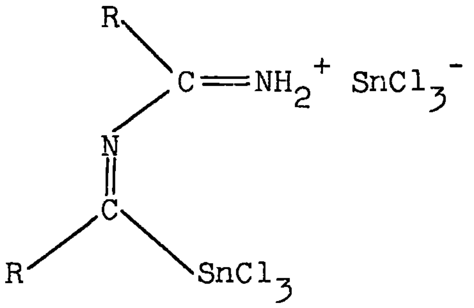
Infra-red (cm^{-1}) (Nujol mull): 2280s, 1415m, 1305w, 1175m, 1150w, 1010w, 970w, 900w, 750sh, 720m, 680m, 455w, 375s, 358s.

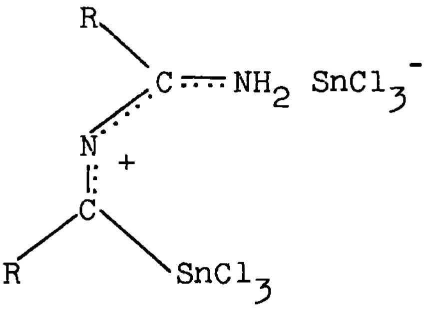
5.3 Results and Discussion

Alkyl and Aryl Nitriles with Tin Dichloride and Hydrogen Chloride

5.3.1 Preparative and Stability Aspects

The reaction of $SnCl_2$ and HCl with alkyl or aryl nitriles yields products of the general formulae shown in Figure 5.2.a,b. The precise electronic structure cannot be discussed at the present stage of investigation. For simplicity the butadiene type structure, Figure 5.2.a, will be considered as representative.





R = Me, Et, Bu^t, Ph

Figure 5.2.a

Figure 5.2.b.

Variation of R has considerable effect on the thermal stability of the compounds.

The methyl and tertiary butyl derivatives, III and V, darkened in colour after separation and difficulty was encountered in obtaining satisfactory infra-red spectra, the compounds becoming waxy and less easy to mull. This may have been due to loss of HCl or more probably further rearrangement (see section on mechanistic consideration).

Also whereas the ethyl and phenyl compounds were stable for several days in d_6 dimethyl sulphoxide, the methyl derivative decomposed immediately and the tertiary butyl in about 1 hr. The decomposition products were not characterized.

5.3.2 Structural and Spectroscopic Aspects

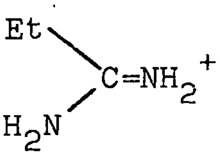
(i) Analysis:

The elemental analysis (Table 5.1) are consistent with the formation of 1:1 adducts between trichlorostannane, $HSnCl_3$, and a nitrile. However analyses for tin in oxidation state II (see Appendix A for experimental details) show only half the tin to be in this state. Analyses for total tin were uniformly poor suggesting that the analytical method was inaccurate (see Appendix A for discussion). We therefore consider that the tin II is present either as $SnCl_2$ or, more likely, $SnCl_3^-$.

(ii) Mass Spectra:

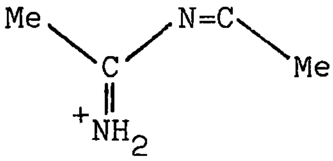
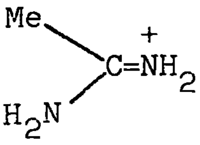
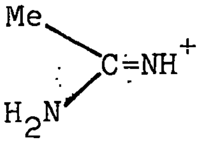
The spectra are summarized and assigned in Table 5.2 and shown graphically in Figures 5.3-5.7. None of the compounds III-VI showed parent ions in their mass spectra. The highest mass peaks are due to $SnCl_3^+$ or $SnCl_4^+$

TABLE 5.2.A Tin Containing and other significant peaks in the mass spectrum of compound IV (R = ethyl) †

Ion	m/e	Relative Intensity Low Temp.	Relative Intensity High Temp.
$SnCl_4^+$	260	0	3.16
$SnCl_3^+$	225	5.14	31.18
$SnCl_2^+$	190	0	34.27
$SnCl^+$	155	0	69.80
Sn^+	120	0	9.83
$(Et\text{-}CN)_2^+$	110	0	0.56
	73	20.70	5.34
$EtCNH_2^+$	57	25.44	4.99
$EtCNH^+$	56	32.00	8.29
HCl	36	72.53	100
?	238	9.74	5.27
?	218	10.42	3.79

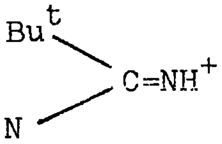
† See also Figures 5.3.a,b

TABLE 5.2.B. Tin containing and other significant peaks in the mass spectrum of Compound III (R=methyl) †

Ion	m/e	Relative Intensity
$SnCl_4^+$	260	3.50
$SnCl_3^+$	225	4.78
$SnCl_2^+$	190	3.00
SnCl	155	10.98
Sn^+	120	3.96
	84	2.00
	59	67.72
	58	41.06
$MeCNH^+$	42	100
HCl	36	70.71

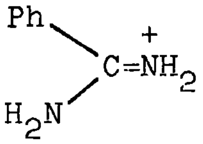
† See also Figure 5.4

TABLE 5.2.C. Tin containing and other significant peaks in the mass spectrum of compound V (R = t-Butyl)†

Ion	m/e	Relative Intensity
$SnCl_3^+$	225	2.50
$SnCl_2^+$	190	3.00
$SnCl^+$	155	16.60
Sn^+	120	17.16
	98	6.08
?	86	13.30
Bu^tCNH^+	84	.00
Bu^tCH^+	70	37.81
Bu^{t+}	57	50.72

† See also Figure 5.5.

TABLE 5.2.D. Tin containing and other significant peaks in the mass spectrum of the compound VI (R=Ph)†

Ion	m/e	Relative Intensity
$SnCl_3^+$	225	4.23
$SnCl_2^+$	190	1.17
$SnCl^+$	155	4.18
	121	2.53
Sn^+	120	1.51
$PhCNH_2^+$	105	80.00
PhCNH	104	100
PhH	78	35.72
HCl	36	48.32

† See also Figure 5.6.

TABLE 5.2.E. Tin containing and other significant peaks in the mass spectrum of tri n-Butyl tin chloride

Ion	m/e	Relative Intensity
$Bu^n_2SnCl^+$	269	0.82
Bu^nSnCl^+	212	0.64
$SnCl^+$	155	0.54
Sn^+	120	0.32
Bu^{n+}	57	2.30

TABLE 5.3 NMR Spectra of Products from the Reaction of RCN with HCl and $SnCl_2$[a]

R	Absorptions
Me	Sample decomposed
Et	1.15t (J=7.5Hz)(3), 1.37t(J=7Hz)(3), 2.66q(J=5.25Hz)(2) 4.44q(J=5.25Hz)(2), 7.20t(J=50.7Hz)(2)
Bu^t	1.03t(J=7Hz)(9), 7.28t(J=5 2 Hz)(2)
Ph	7.13t(J=52Hz)(2), 7.70-7.80(∿20)

(a) Recorded in d_6 dimethyl sulphoxide with internal TMS standard (δ=0)

(b) Relative intensities and coupling constants in parentheses, t=triplet, q=quartet.

Figure 5.3a

Low Temperature Mass Spectrum of $C_3H_6NSnCl_3$

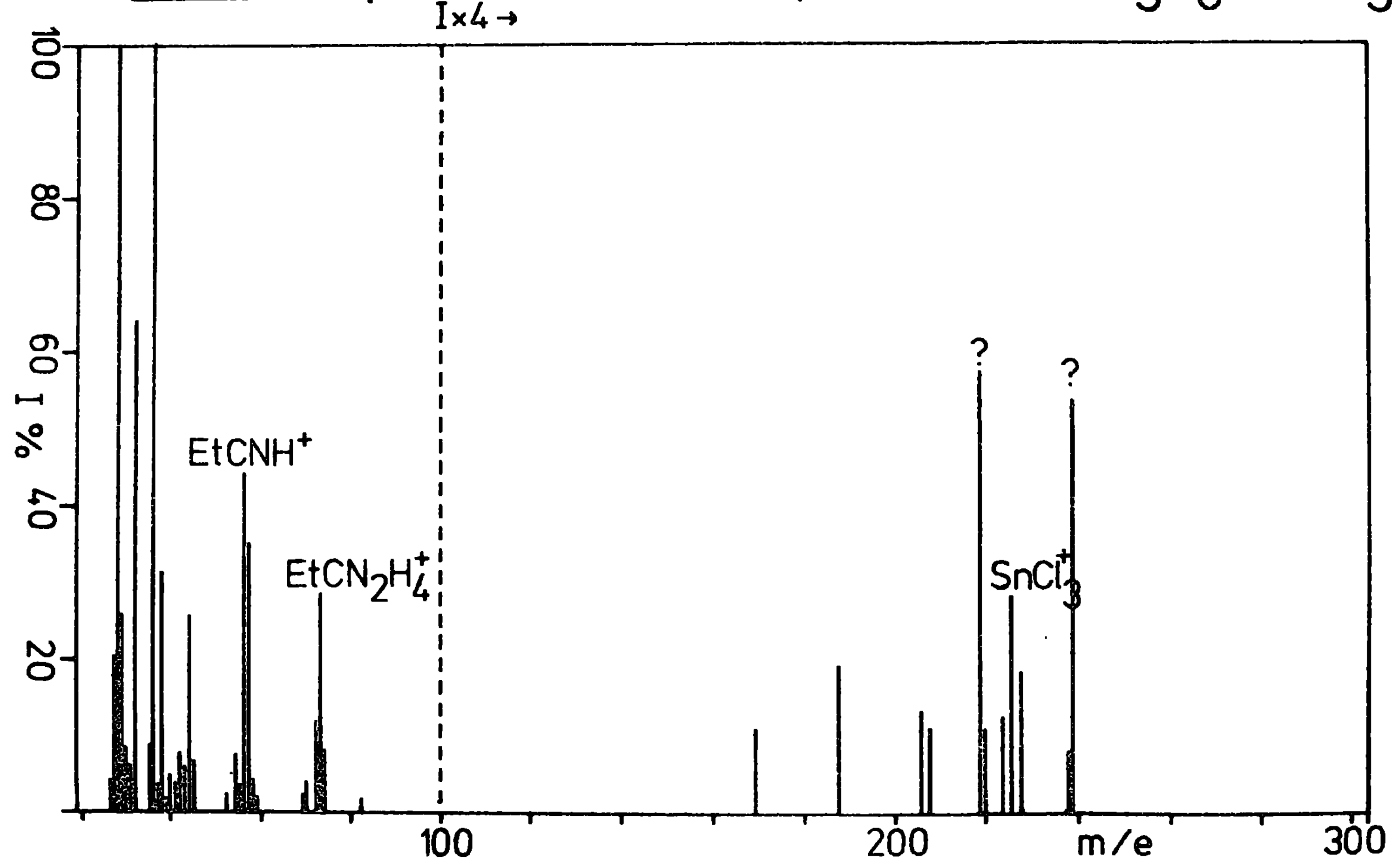


Figure 5.3b

High Temperature Mass Spectrum of $C_3H_6NSnCl_3$

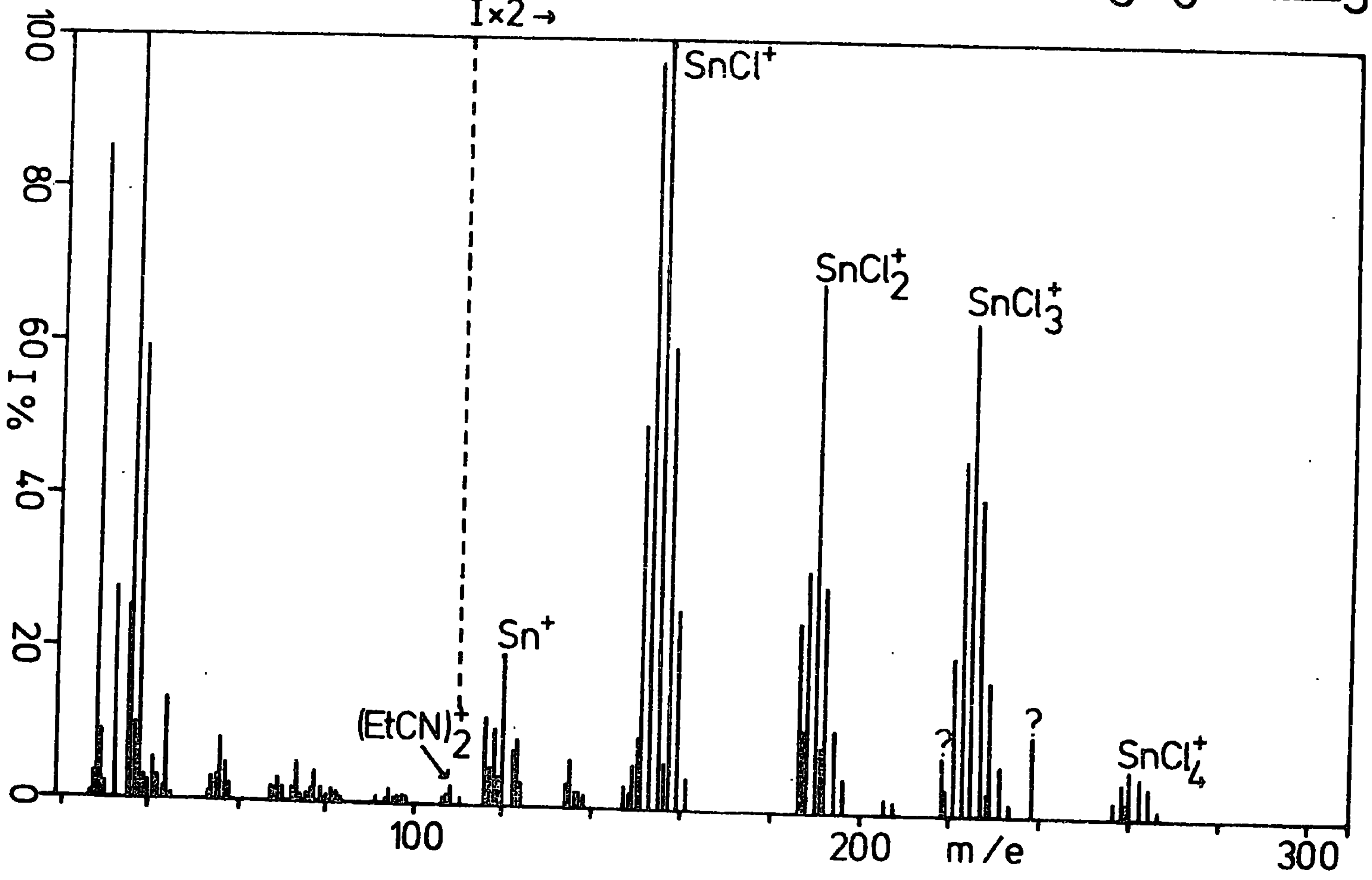


Figure 5.4

Mass Spectrum of $C_2H_4NSnCl_3$

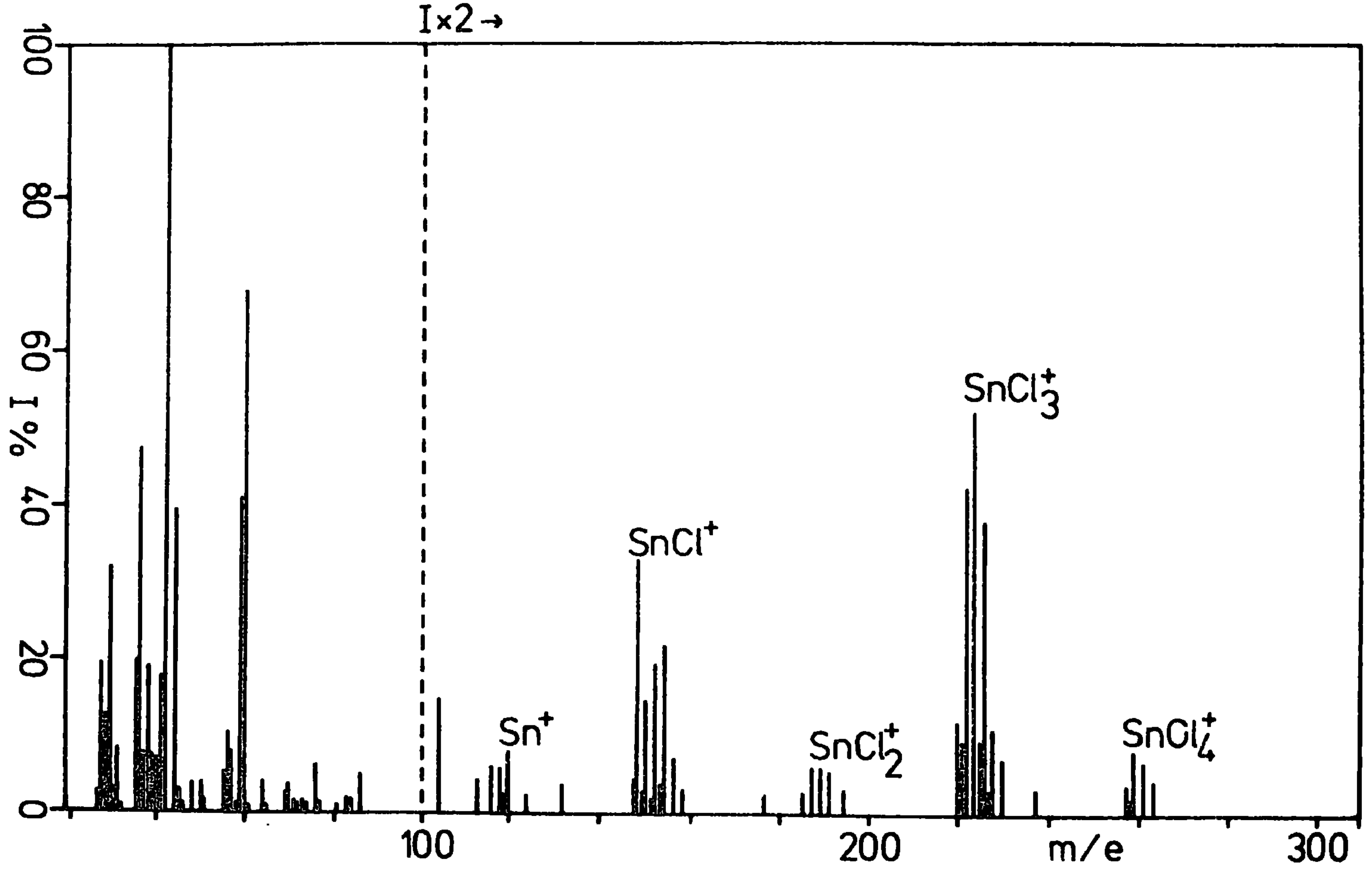


Figure 5.5

Mass Spectrum of $C_5H_{10}NSnCl_3$

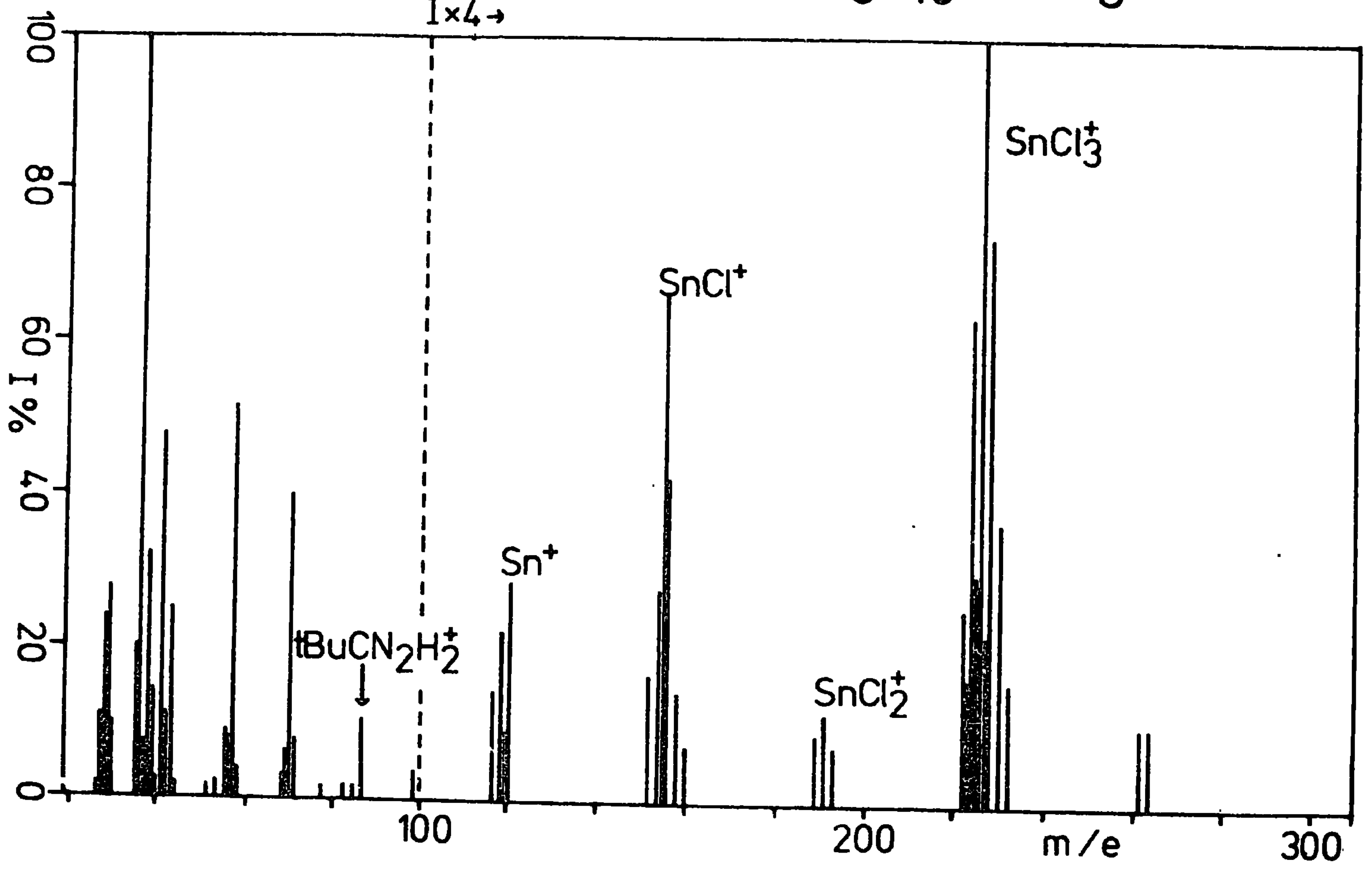
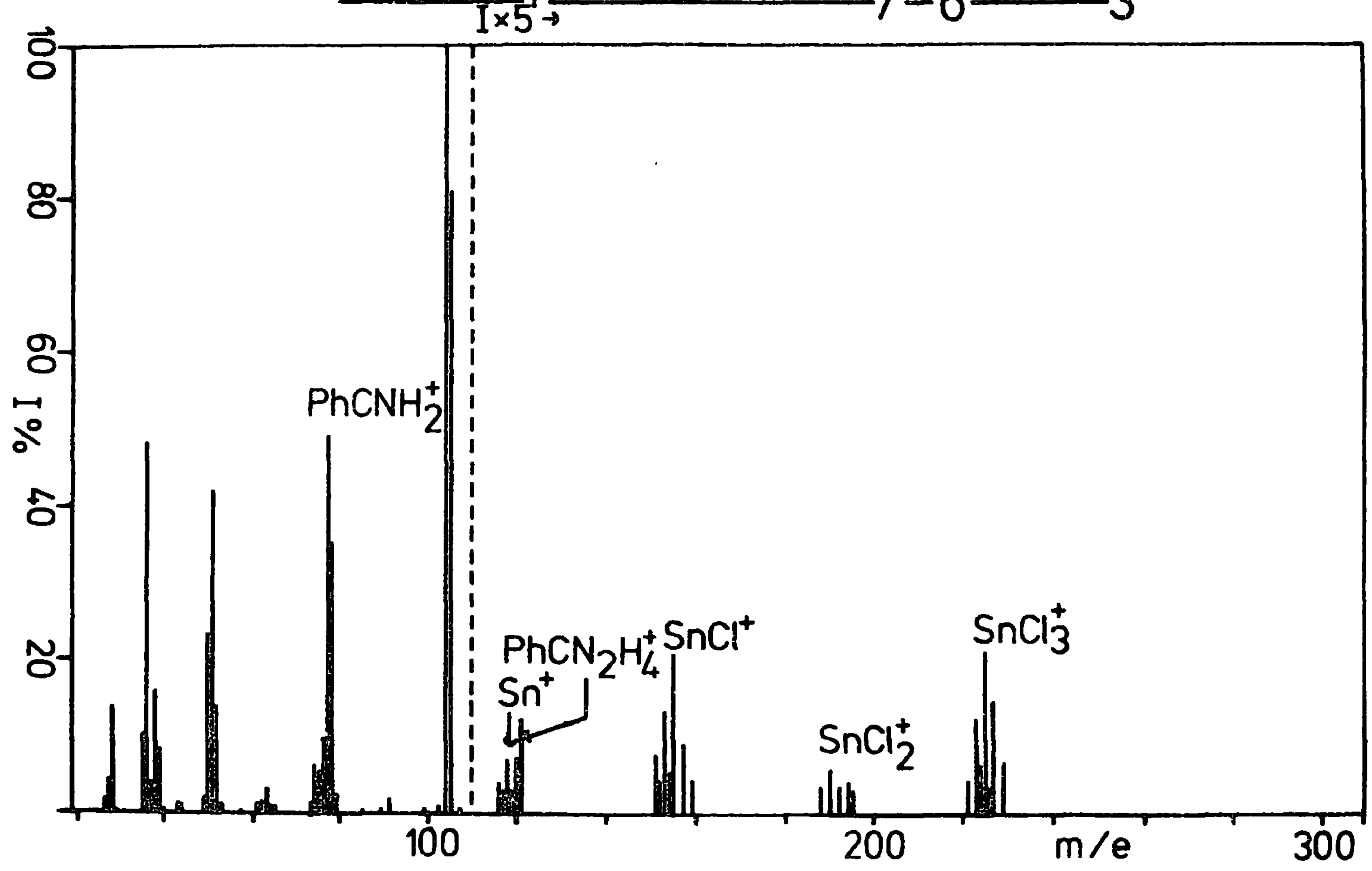


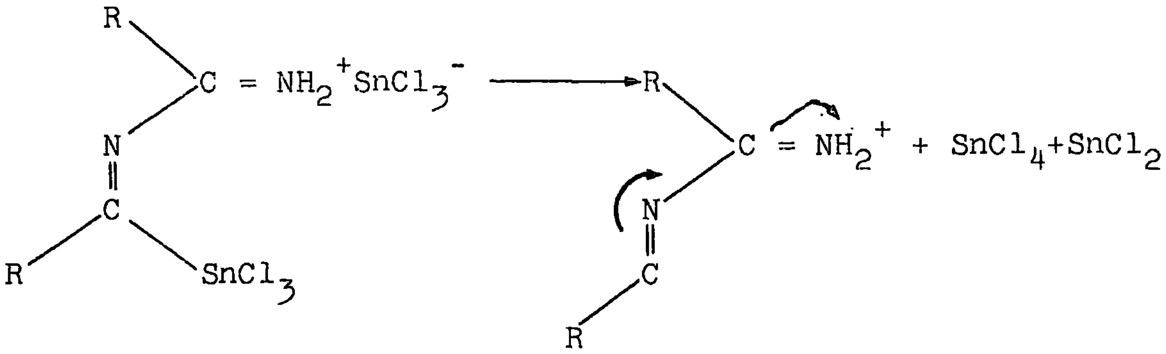
Figure 5.6

Mass Spectrum of $C_7H_6NSnCl_3$

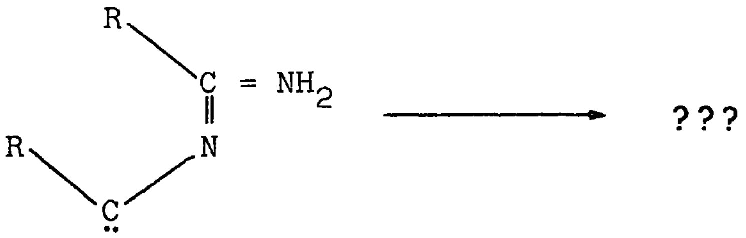


the latter being attributable to an ion recombination reaction (equation 5.6) on decomposition of the sample on the mass spectrometer probe by elimination of $SnCl_4$ and $SnCl_2$ to give a carbenoid species (equation 5.7).

$$R\ SnCl_3 \longrightarrow R^- + SnCl_3^+ \xrightarrow{+Cl^-} SnCl_4 \xrightarrow{-e} SnCl_4^+ \qquad (5.7)$$



(5.8)



Ion-ion reactions would be expected to be inlet pressure dependent. However this is difficult to control when admitting a solid to the mass spectrometer. An elimination reaction, equation 5.8, would be expected to be temperature dependent. Figures 5.3.a and b. show two separate scans for the ethyl compound after 4 mins. (Figure 5.3.a) in the ion chamber and after 8 mins. (Figure 5.3.b). At the earlier time at lower temperature, there are no peaks due to $SnCl_4^+$ and only weak peaks due to $SnCl_3^+$. As the probe warms up however (Figure 5.3.b) peaks due to $SnCl_4^+$ become evident.

Peaks at m/e 238 and 218 in the low temperature scan do not contain tin or chloride. They may be due to ion-molecule or ion-ion combinations or possibly from the reaction of the carbene species proposed above.

Loss of $SnCl_4$ is also observed for R = Me. The general breakdown pattern of loss of organic fragments before halide ions is typical of organotin compounds as shown in Table 5.2f which lists the fragmentation pattern of tin(n-butyl)tin chloride (this work) and also in section 5.4.1 where the mass spectrum of β cyanoethyl tin trichloride is discussed.

Only for R = Me (Figure 5.4, Table 5.2b) is a peak corresponding to an intact organic backbone, $MeCN(Me)C{:}NH_2^+$ observed. In all other cases the highest mass organic fragment is $R - \underset{NH_2}{\underset{/}{C}}{:}NH_2^+$, also an ion molecule product. Lower mass peaks are consistent with the breakdown thereof.

5.3.3 N.M.R. Spectra

N.M.R. spectra were recorded in d_6 dimethyl sulphoxide, the only solvent in which the compounds were found to be soluble. They were insoluble in less polar solvents such as $CDCl_3$, CCl_4 or d_8-toluene.

The methyl derivative appeared to decompose in solution. The solution turned brown over a period of 5 mins. and the nmr spectrum could not be interpreted due to its complexity. The 60MHz spectrum of the ethyl derivative, Figure 5.8a shows the presence of two magnetically different ethyl groups. Three equal intensely absorptions at 6.33δ, 7.20δ and 8.07δ are assigned as a triplet (J=52Hz) due to coupling between the ^{14}N nucleus (spin=1) and the protons of the $C{=}NH_2^+$ group. This was confirmed by rerecording the spectrum at 90 MHz, Figure 8b, when the coupling constant

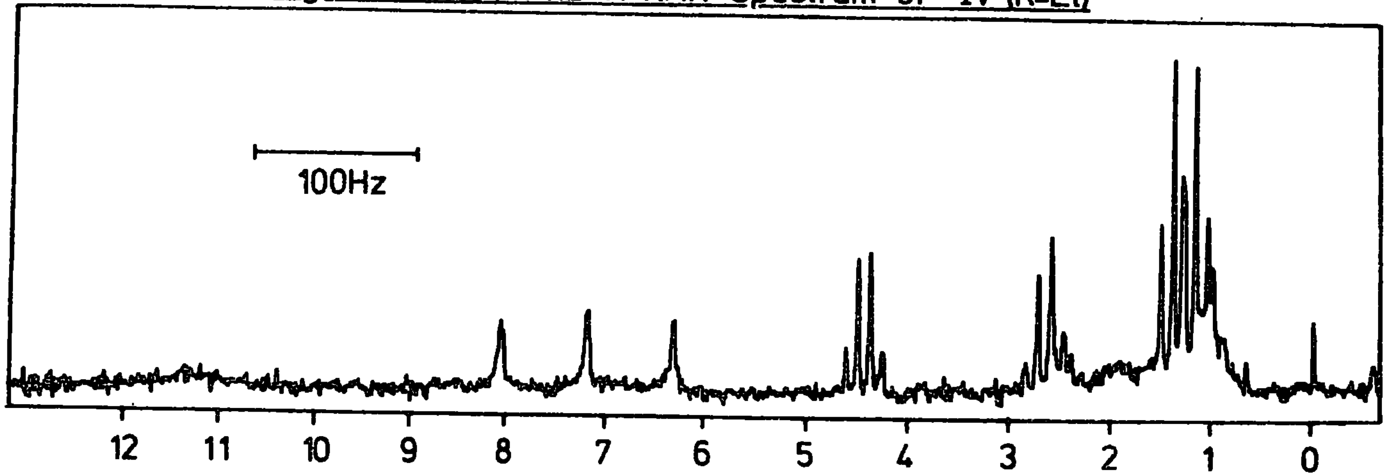


Figure 5.8a.60 Mhz H NMR Spectrum of IV (R=Et)

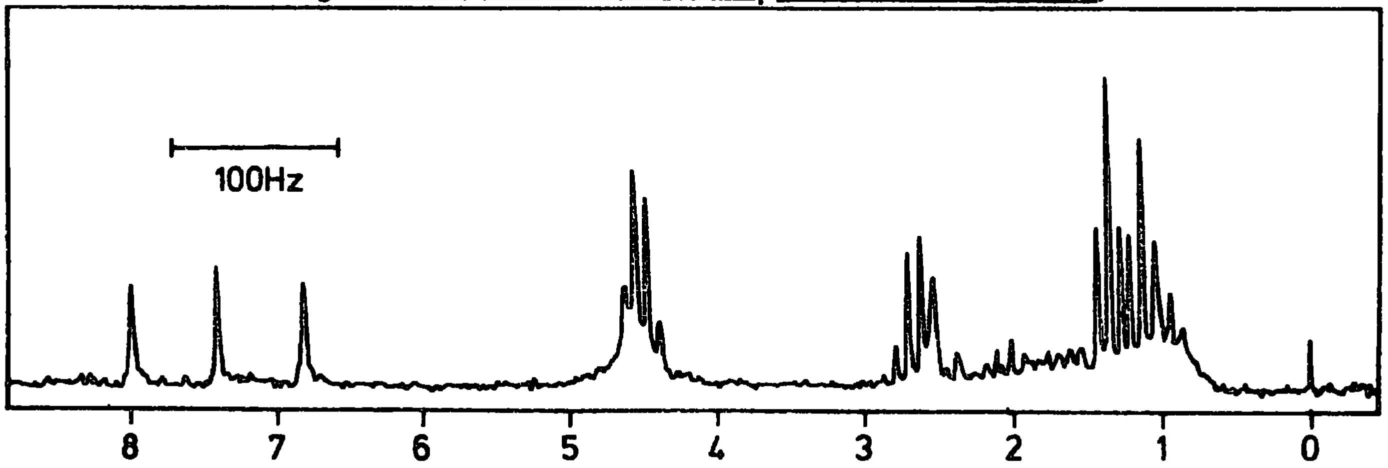


Figure 5.8.b.90 Mhz ^{1}H NMR Spectrum of IV (R=Et)

was found to remain the same. Assignments for all compounds are listed in Table 5.3. The 60MHz spectra of the Bu^t and phenyl compounds show the expected absorptions due to the alkyl or aryl groups. Only one absorption could be resolved probably since the protons in the Bu^t group are more remote from the inductive influence of the electron withdrawing group. The aryl proton absorptions could not be resolved in sufficient detail to extract any structural information. Both the phenyl and t-butyl compounds show equal intensity triplets centred on 7.13δ and 7.28δ respectively, identical to those observed in the ethyl derivative.

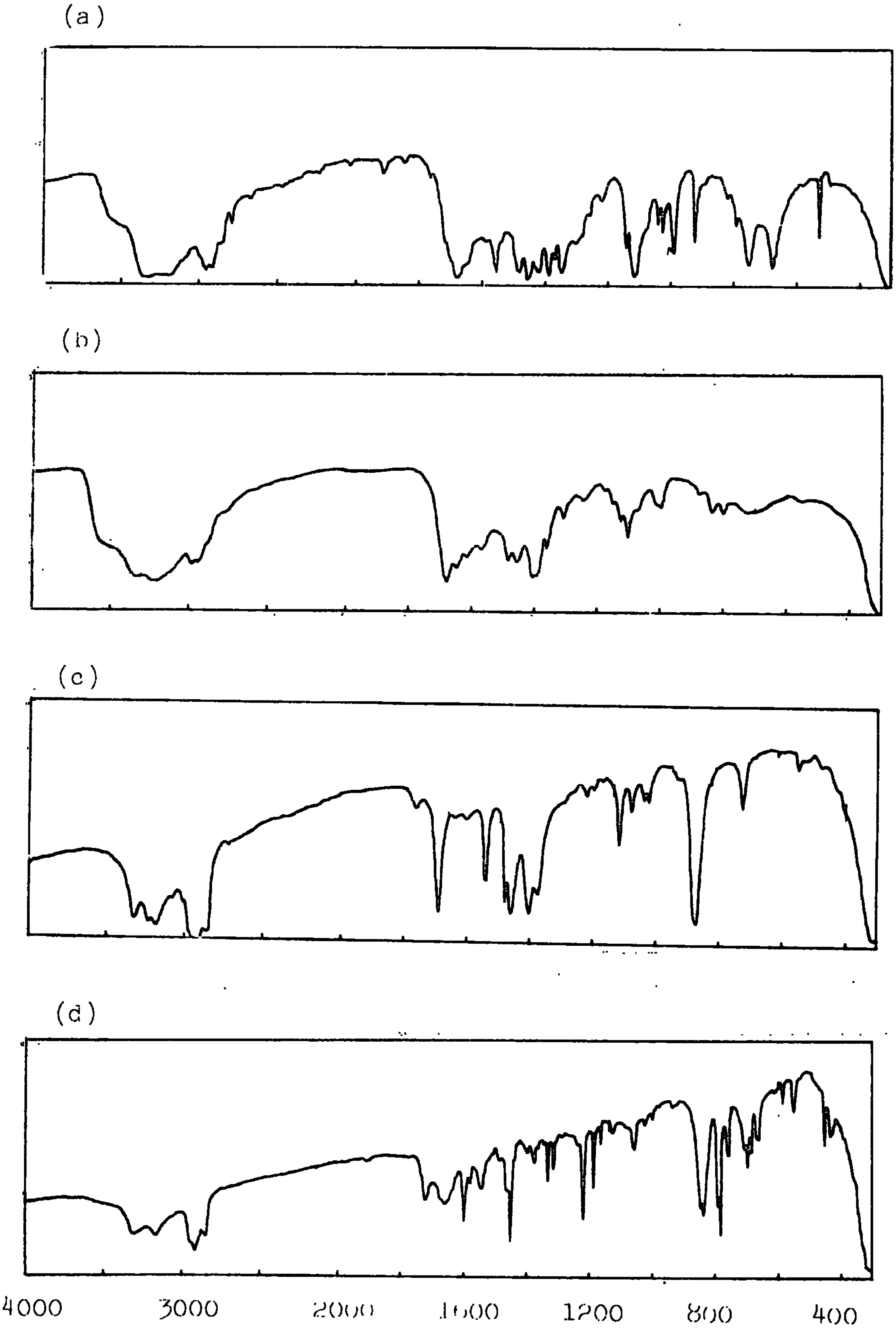
Proton nitrogen coupling is only rarely observed for two reasons. Firstly the nuclear quadrupole of ^{14}N causes the nuclear relaxation time to be increased leading to broadening and coalescence of the lines.[24,25] Secondly the acidity of protons bonded to nitrogen leads to considerable hydrogen bonding and usually facilitates rapid proton exchange which would destroy any coupling if it occurs faster than the n.m.r. time scale. Any hydrogen exchange must therefore be relatively slow. The value of the coupling constants (J=52 Hz) compares with J(^{14}N-H) of 40-68 Hz for dialkylamines or tertiary alkylammonium salts.[22,23]

5.3.4 Vibrational Spectra

The vibrational spectra of the compounds were generally less informative than the other spectra. The compounds were very difficult to mull, insoluble in common infra-red solvents and usually gave poor spectra. Therefore only general structural data could be inferred.

All the spectra (Figures 5.9a-d) showed two or three broad intense peaks in the 3200 cm^{-1} to 3500 cm^{-1} region,

FIGURE 5.9 IR Spectra of (a) III, (b) IV, (c) V, (d) VI



assigned to strongly hydrogen bonded (N-H) vibration. Only two bands would be expected from an NH_2 group, a symmetric and an assymmetric stretch. The third band may be a combination band. Three bands are observed in this region in aniline[26] and several broad intense peaks between 3100 cm^{-1} and 3300 cm^{-1} are found in the spectra of some dialkylamine hydrochlorides[27].

Two types of absorption are expected in the 1480 cm^{-1} to 1700 cm^{-1} region. We expect the (C=N) double bond stretch and the $\delta(NH_2)$ scissoring. All the compounds show at least 3 absorptions in this region. If Figure 5.2.a is a good representation of the true structure then we would expect only 3 absorptions in this region, two $\nu(C{=}N)$ and one $\delta(NH_2)$. However if the delocalised bonding description, Figure 5.2.b, contributes to the bonding then one would expect more absorptions in this region. Therefore the non-delocalized description, Figure 5.2a, is tentatively put forward as the preferred structure. Bands due to the $SnCl_3$ groups are expected to be in the region 200-400 cm^{-1}.[28,29] This is however outside the KBr region recorded.

5.3.5 Mechanistic Aspects

The mechanism of formation of hydrostannated nitrile dimers can be considered in three independent stages:

(a) the nature of the HCl/$SnCl_2$ reaction;
(b) the reaction of the product from (a) with nitriles; and
(c) dimerization.

(a) The nature of the HCl-$SnCl_2$ system:

The hydrogen chloride tin dichloride system has been extensively studied from its utility in the preparation of organotin chlorides.[4-13] However only very recently has the system been studied in detail. Dutch workers[30] have shown that the reaction can be crudely represented by equation 5.9.

$$nHCl + SnCl_2 + mEt_2O \rightleftharpoons \underset{(I)}{H_nSnCl_{2+n}.mEt_2O} \qquad (5.9)$$

(I) separates from ethereal solution as a yellow oil. The Dutch also found the 'H nmr to show the presence of a strongly deshielded proton between 10.8 and 12.8 ppm, depending on experimental conditions (in contrast to 6.8 ppm for $HCl.nEt_2O$) and the interaction of the proton with the co-ordinated ether in I is reflected in the chemical shifts of the ethyl groups.

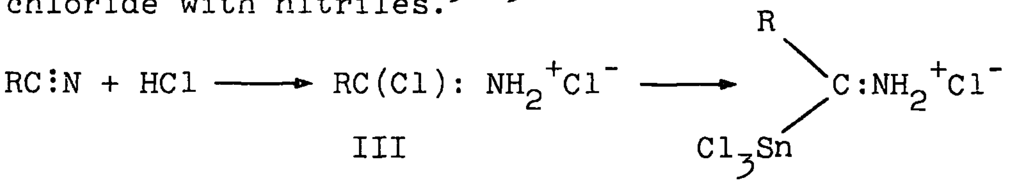
The absence of a band between 1700 cm^{-1} and 2200 cm^{-1} in the infra-red confirmed that a covalent tin hydrogen bond was not present.

They found the ^{119}Sn Moessbauer parameters of I to be more consistent with a tin II species than a tin IV species and most closely resembled data obtained from triligand stannates. Consequently they conclude that I consists of ionised dihydrogen tetrachlorostannate II, equation 5.10.

$$H_2SnCl_4 + 2Et_2O \longrightarrow 2Et_2{}^+OH + SnCl_4{}^{2-} \qquad (5.10)$$

(b) The mechanism of reaction of dihydrogen tetrachlorostannate II with nitriles:

It would appear reasonable to draw the analogy between the reaction of $HSnCl_3$ with olefins and with nitriles. According to workers of Akzo Chemie[8,9] the formation of alkyl tin from an olefin, HCl and $SnCl_2$ is due to the addition of Sn-H across the unsaturated linkage as has been established in the reaction of Et_3SnH with ACN.[31-33] However in view of the considerations in the preceding section this seems unlikely. An alternative possibility would be addition of tin dichloride to a C chloro alkyl imidoyl salt (III), equation 5.11, as formed from the reaction of hydrogen chloride with nitriles.[34-36]

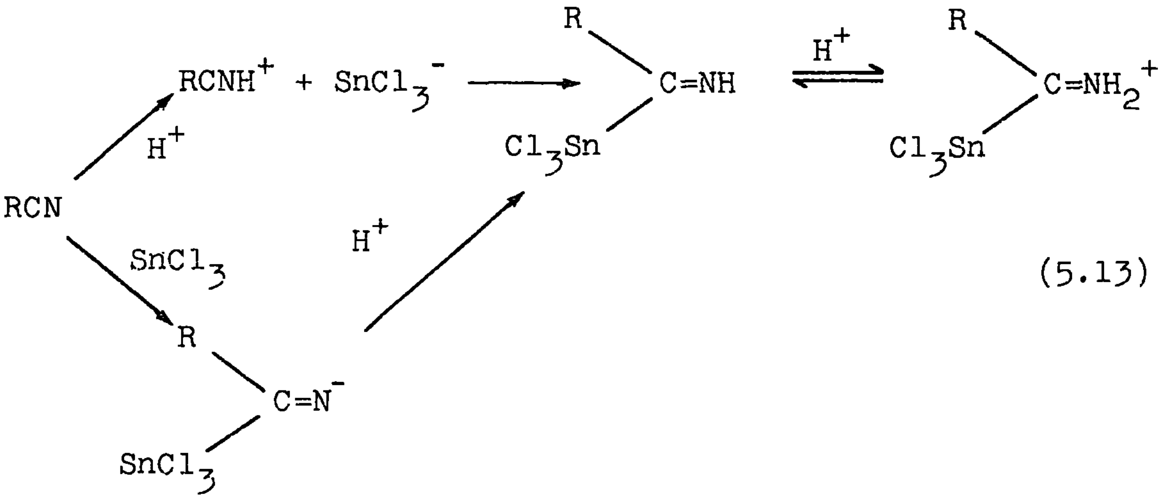


$$RC{\vdots}N + HCl \longrightarrow \underset{III}{RC(Cl){:}\ NH_2^{+}Cl^{-}} \longrightarrow \overset{R}{\underset{Cl_3Sn}{>}}C{:}NH_2^{+}Cl^{-} \qquad (5.11)$$

However no imidoyl chloride dimerization (*vide infra*) products were observed in our systems and also it has been found that tin dichloride does not react with β-Cl methyl propionate[30], equation 5.12.

$$SnCl_2 + ClCH_2CH_2CO_2Me \not\longrightarrow Cl_3SnCH_2CH_2CO_2Me \qquad (5.12)$$

Therefore we consider the most probable mechanism to be a 1,2 addition involving initial protonation of the nitrile to give a nitrilium salt followed by nucleophilic attack by trichlorostannate II to give an alkyl trichlorostannyl imine or iminium salt, equation 5.13.

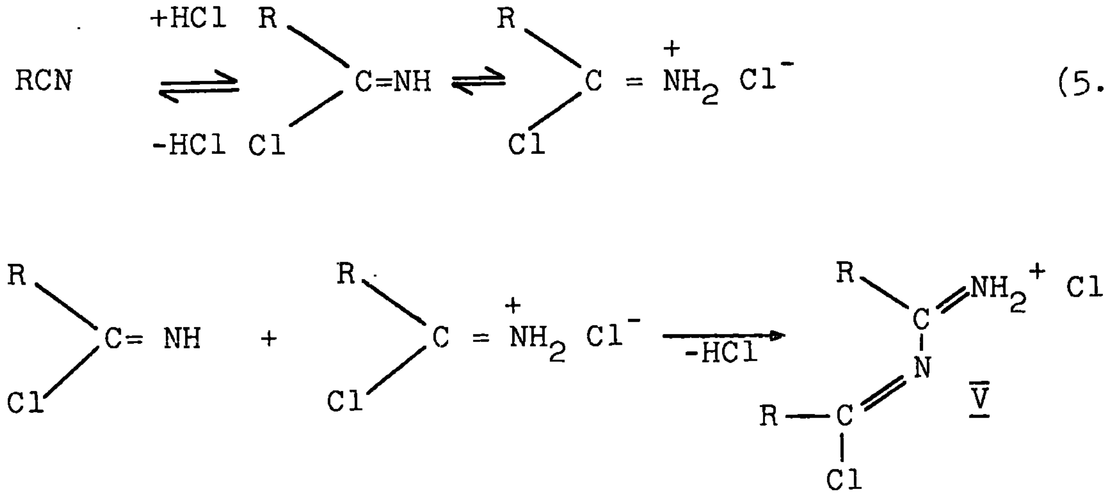


(5.13)

(c) The dimerization of alkyl trichlorostannyl imine:

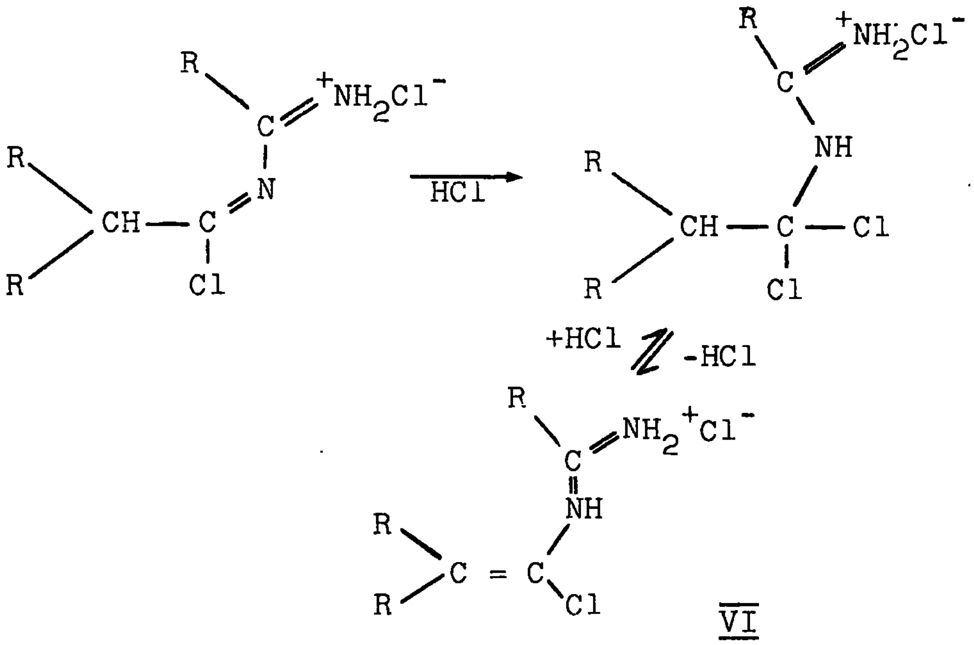
The literature is abundant with the reaction of hydrogen halides with nitriles. Schaeffer[37] has reviewed the subject and recently in a series of papers[35,36,38,39] a Japanese group have surveyed and reinvestigated the reactions of hydrogen chloride with alkyl and aryl nitriles.

Imidoyl chlorides dimerize under relatively mild conditions by displacement of a chloride ion by a second molecule of iminium base acting as a nucleophile, yield N(alkyl chloro methylene) alkyl amidium salts, V, equation 5.14.



(5.14)

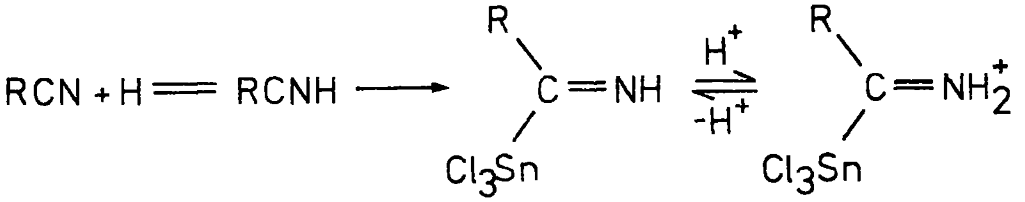
The simplest systems are those having no α hydrogen such as Me_2N,[40] Ph,[36] RC_6H_4,[36] RS.[36] When substituents contain an α hydrogen the product V undergoes rearrangement[35] to give an N(α chloroalkenyl) alkyl amidine salt VI, equation 5.15.



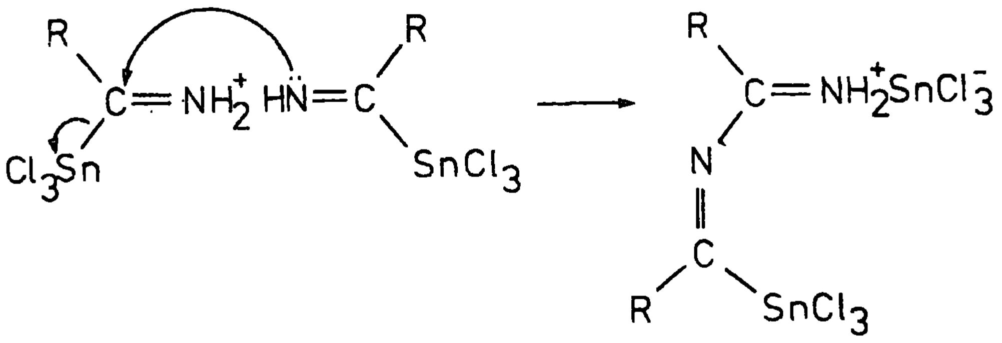
(5.15)

The dimerization of alkyl trichlorostannyl iminium salts may be analogous to equation 5.14 although one can postulate several plausible reaction pathways as summarized in Equations 5.16-19. The reaction terminates at this stage for all the derivaties. One reason that the derivatives with α hydrogens do not undergo further reaction (equation 5.13) may be that the trichlorostannate II group is not as good a leaving group as the chloride ion, thus rendering equation 5.19 very slow.

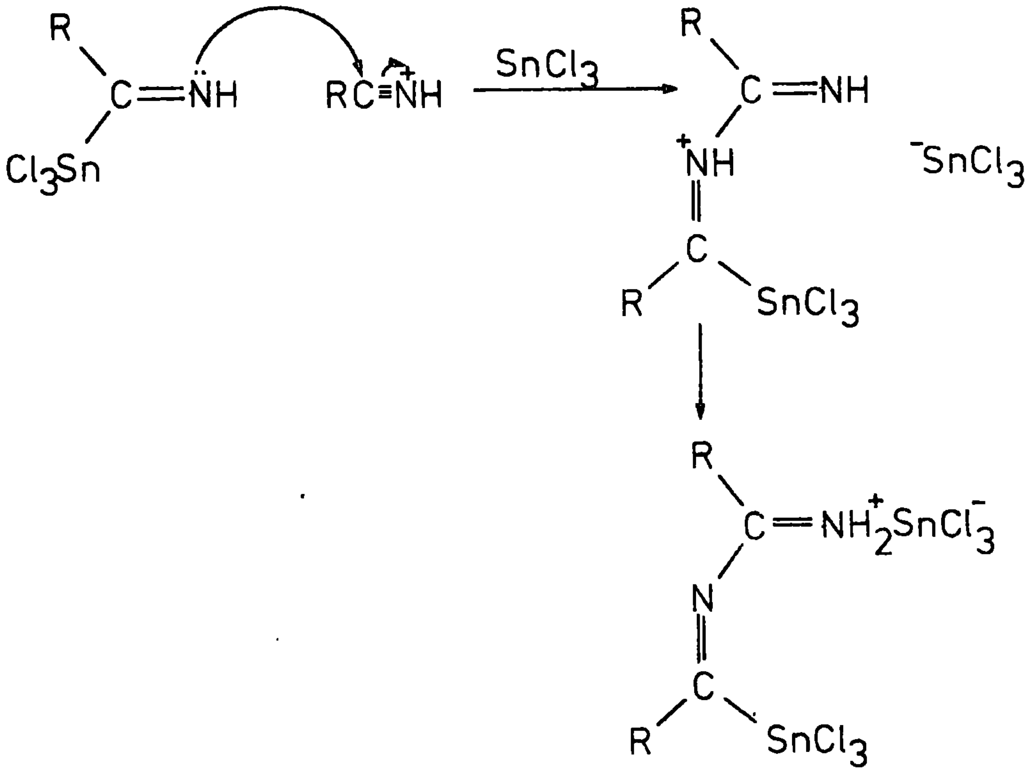
We also favour equation 5.18 to equation 5.17 for the same reason.



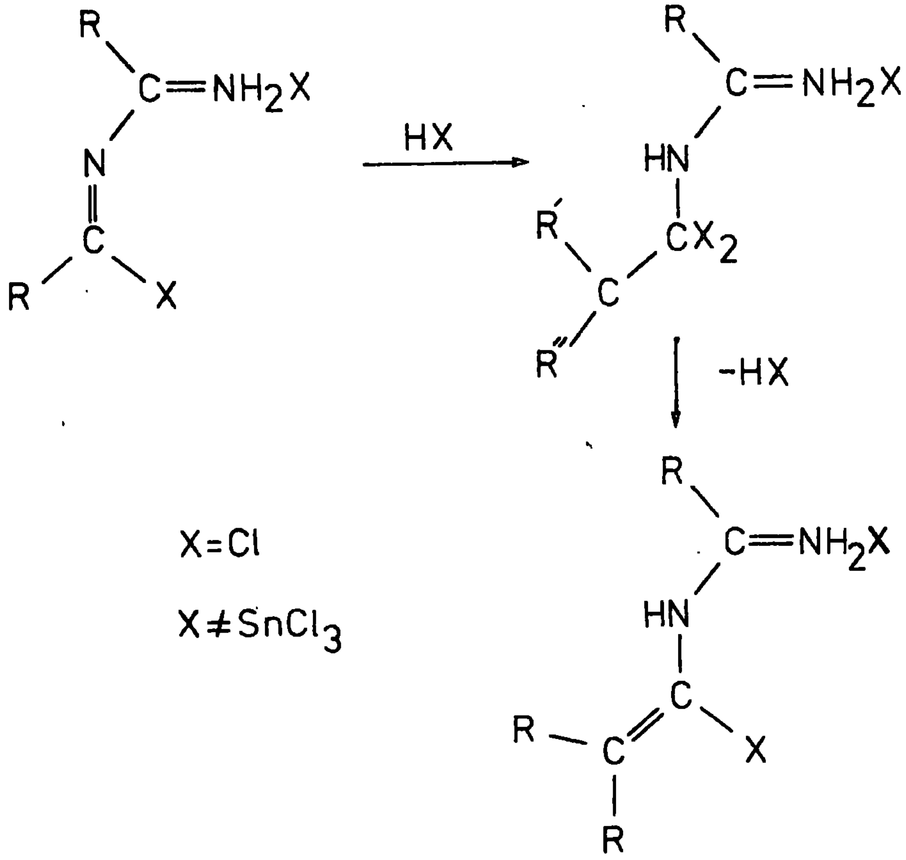
5.16



5.17



5.18



X=Cl

X≠SnCl$_3$

5.19

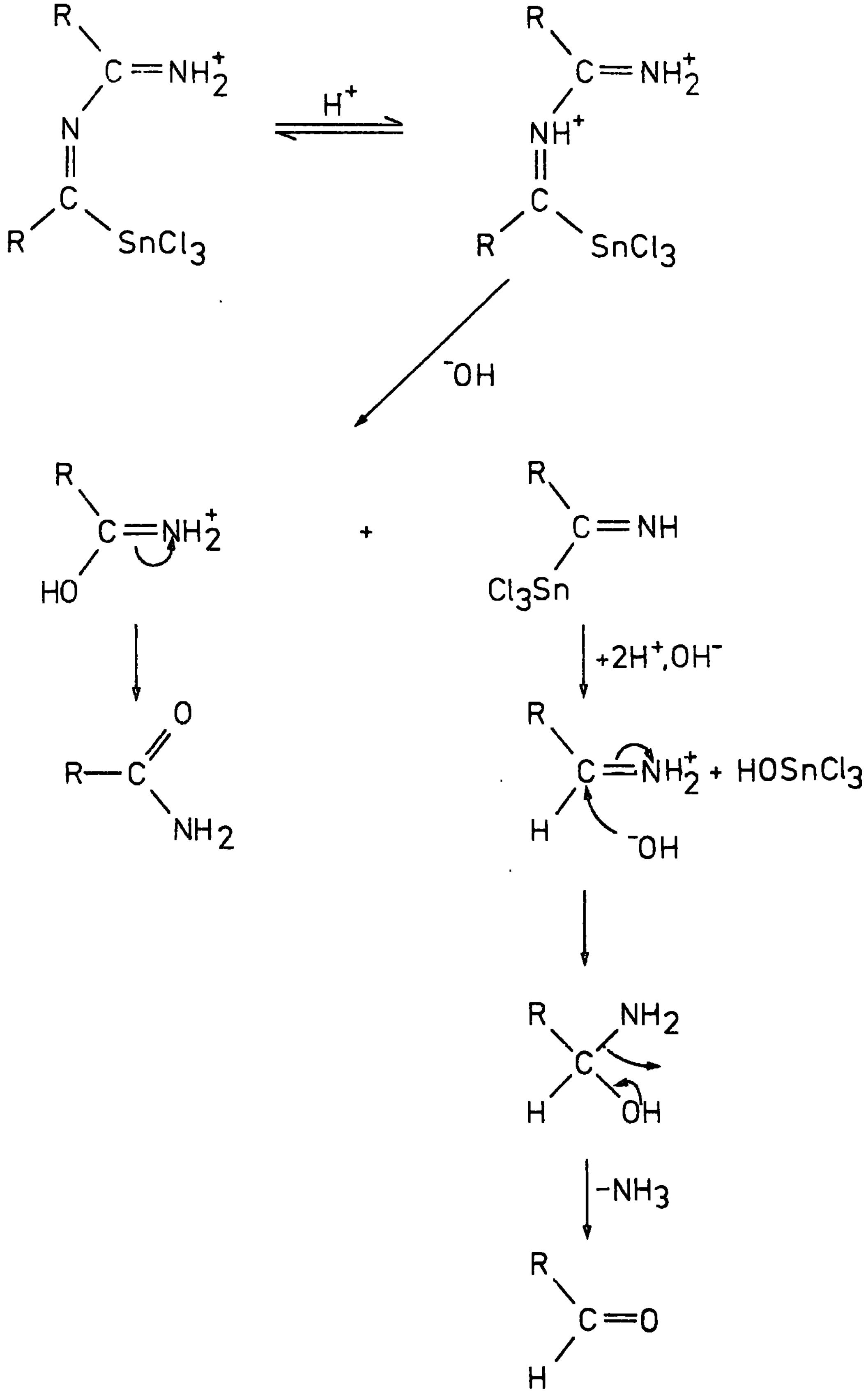
5.3.6 Aspects Relevant to the Stephens Reaction

The compounds described in this chapter do not form any part of previously proposed mechanisms of the Stephens' reaction. The reaction has been considered to proceed by the reduction of an imidoyl chloride to an aldimine. Hydrolysis of the aldimine yields the aldehyde (Equation 5.20).

$$\left.\begin{array}{r}
RCN + HCl \longrightarrow RC(Cl) = NH \\
RCCl = NH + SnCl_2 + HCl \longrightarrow RCH = NH.HCl.SnCl_4 \\
RCH = NH.HCl.SnCl_4 + H_2O \longrightarrow RCHO + NH_4Cl + SnCl_4
\end{array}\right) \quad (5.20)$$

Whilst this reaction mechanism cannot be discounted on the basis of this work it suggests that the predominant reactive species is $H^+ + SnCl_3^-$ as opposed to HCl. The formation of primary amides in the Stephens' reaction has been suggested as being due to the hydrolysis of $RCN.SnCl_2$ adduct. However no nitrile adducts of $SnCl_2$ have been isolated (this work). The amides will arise from the hydrolysis of the dimer II in the following scheme, (overleaf).

Experiments are in progress to confirm that the products of hydrolysis of II are indeed aldehyde and dimer is 1:1 ratio.



H+
-OH
+
+2H+,OH-
+ HOSnCl3
-OH
-NH3

5.4 Results and Discussion of the reaction of ACN with Tin Dichloride and Hydrogen Chloride

Whilst $SnCl_2$ and HCl are known to add to α, β unsaturated carbonyl compounds to yield (β carbomethoxy) ethyl tin trichloride[9] the reaction with ACN has not previously been described. The product from this reaction, equation 5.21, β cyanoethyl tin trichloride, is believed to be a new compound.

$$HCl + SnCl_2 + ACN \longrightarrow NCCH_2CH_2SnCl_3 \qquad (5.21)$$

5.4.1 Structural and Spectroscopic Aspects

The mass spectrum of β cyanoethyl tin trichloride is shown in Figure 5.10 and the significant peaks are assigned in Table 5.4. Most noticeable in contrast to the mass spectra of the N(trichlorostannyl alkyl methylene) amidinium salts is the presence of tin containing organic fragments. No parent ion is observed but a P+1 peak at m/e 280 corresponds to the protonated parent. This protonation in the mass spectrometer is common amongst nitriles and is due to abstraction of a hydrogen atom by the molecular ion.[41] The infra-red spectrum, Figure 5.11 shows all the expected features. The nitrile absorption at 2280 cm^{-1} is characteristic of an organic nitrile. Other bands assigned to the organic residue are $\delta(CH_2)$ (scissor) at 1415 cm^{-1} and $\tau(CH_2)$ (twist) and $\omega(CH_2)$ (wag) at 1305 cm^{-1} and 1175 cm^{-1}. Bands at 358 cm^{-1} and 375 cm^{-1} correspond to $\nu(Sn\text{-}Cl)$[28] and $\nu(Sn\text{-}C)$.

When the compound was exposed to air and the spectrum rerecorded, in addition to the water peaks, the nitrile band became split into two peaks at 2280 cm^{-1} and 2225 cm^{-1}. This suggests that the nitrile group is coordinated

Figure 5.10

Mass Spectrum of $NCCH_2CH_2SnCl_3$

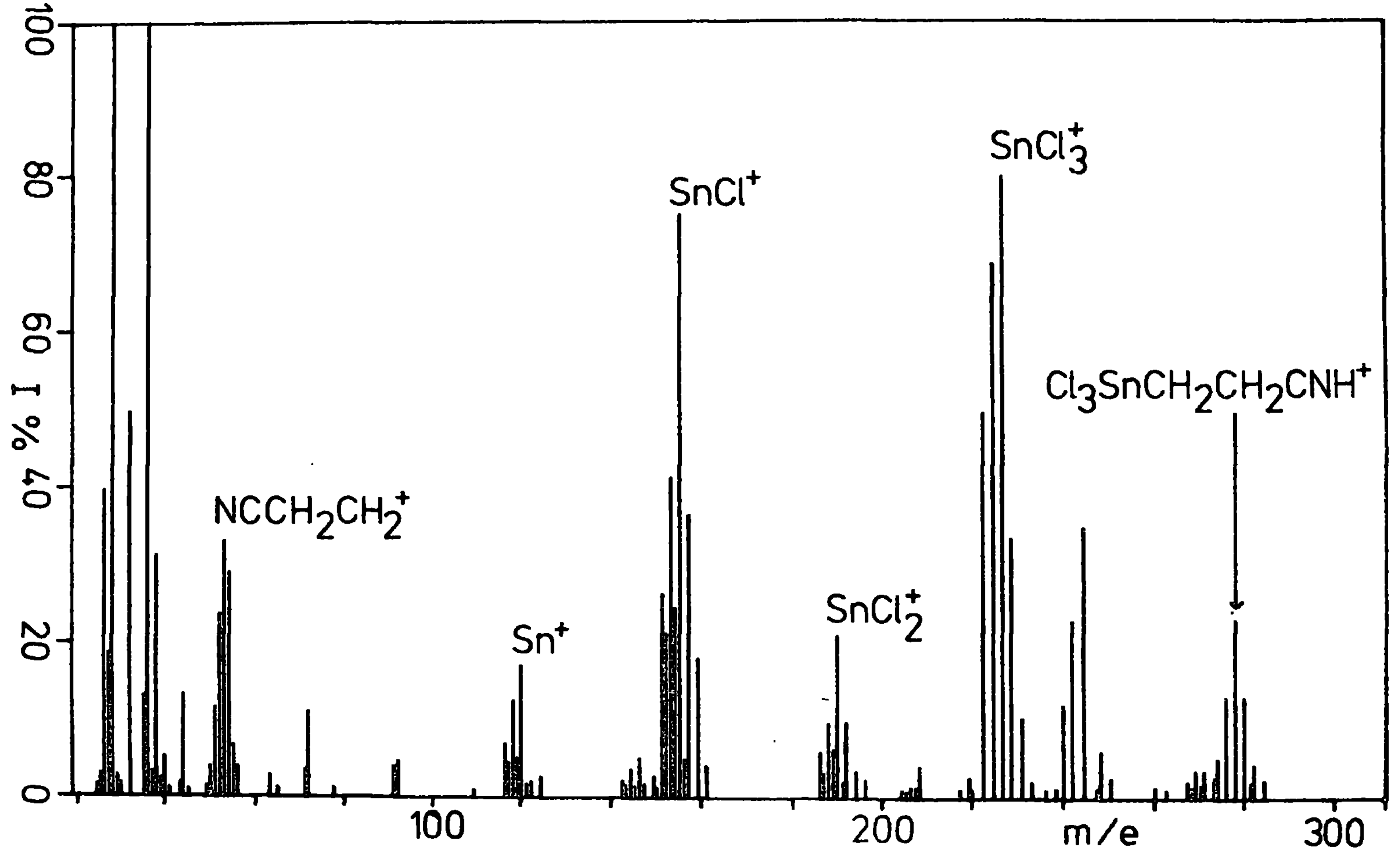
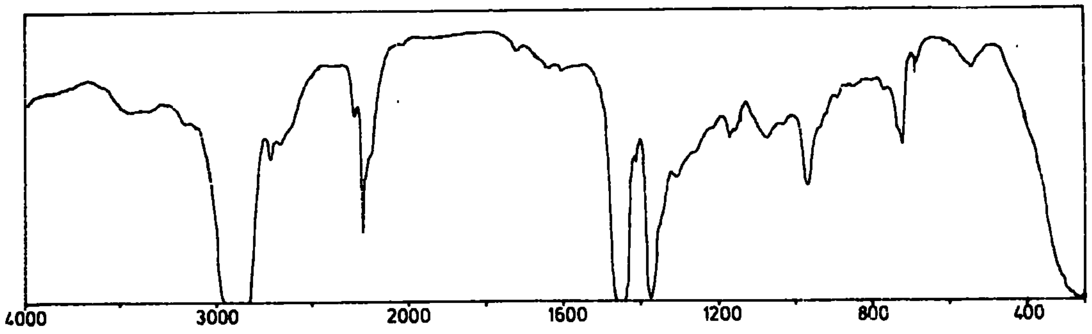


TABLE 5.4 Mass Spectrum of β cyanoethyl tin trichloride

Fragment	m/e	Intensity
$\overset{+}{H}NCCH_2CH_2SnCl_3$	280	6.03
$SnCl_3^+$	225	31.51
$NCCH_2CH_2SnCl_2^+$	245	16.0
$SnCl_2^+$	190	9.62
$SnCl^+$	155	34.42
Sn^+	120	7.85
$NCCH_2CH_2^+$	54	13.31
HCl	36	46

FIGURE 5.11 IR Spectrum of β cyanoethyl tin trichloride



in the solid. Thus uptake of a Lewis base stronger than the nitrile will displace the nitrile from coordination and cause a drop in ν(C≡N). In a non-coordinating solvent, benzene, ν(C≡N) was found to occur at 2284 cm^{-1} whilst in a coordinating solvent, THF at 2242 cm^{-1}, confirming that ν(C≡N) is dependent on the coordinating power of the solvent, the same effect has been observed in β cyanoethyl tin tribromide[42] and was attributed to the formation of a dimeric molecule in non-coordinating environments. This proposal is consistent with our data although a chain structure in the solid is equally plausible. Unfortunately β cyanoethyl tin trichloride is hardly soluble in benzene which prevents the simple cryoscopic determination of molecular weight. The ^1H 90 MHz nmr spectrum is given in Table 5.5.

The spectrum was recorded in d_6.dimethyl sulphoxide and also $CDCl_3$. In each case the high field resonance is assigned to the α methylene group by comparison with R_2SnCl_2[11] and the low field resonance to the β(CH_2) group.

TABLE 5.5 ^1H NMR Spectrum of $NCCH_2CH_2SnCl_3$[(a)]

Solvent	α(CH_2)	β (CH_2)
$CDCl_3$	2.51t(J=8.0Hz)	2.00t(J=8.0Hz)
d_6DMSO	1.73t(J=8.5Hz)	2.73t(J=8.5Hz)

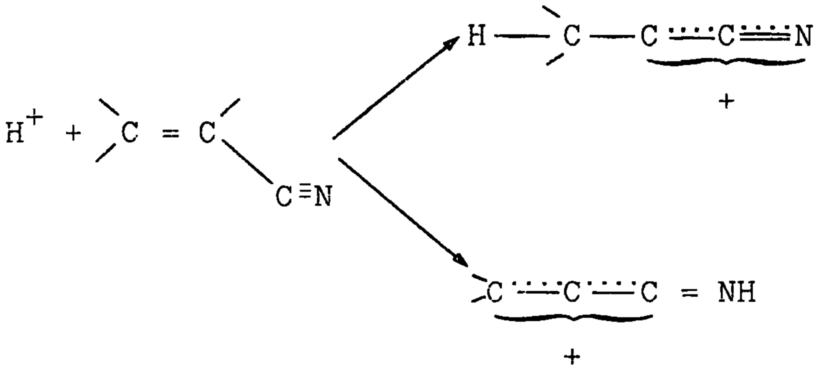
(a) Ref. Internal TMS (δ=0), t=triplet.

It was hoped that recording the spectrum in two solvents of different coordinating power would yield information on the dimeric (or otherwise) nature of the compound. However the differences cannot be reliably interpreted in view of the considerable difference in solvent susceptibility.

5.4.2 Mechanistic Aspects

Considerable discussion has been devoted to the mechanism of hydrostannation by HCl and $SnCl_2$ in section 5.3.5 of this chapter and it will not be repeated here. The additional considerations in this section concern the site of addition (i.e. $>C=C<$ versus $-C\equiv N$) and the orientation of addition.

The preferred site of addition by reagents $H(\delta+) - X(\delta-)$ appears to be consistently the C=C double bond as demonstrated by the reaction of ACN with HX, R_2NH, etc.[43] In general an unsymmetrical reagent, HX, adds to an α, β unsaturated compound so that the hydrogen becomes attracted to the carbon α to the substituent since electrophilic addition proceeds via the most stable carbocation. To rationalize this one consider the α,βunsaturated compound as a conjugated system as follows. Addition of H^+ to an end of a conjugated system is preferred since this yields a resonance stabilized carbocation (equation 5.22 a,b)

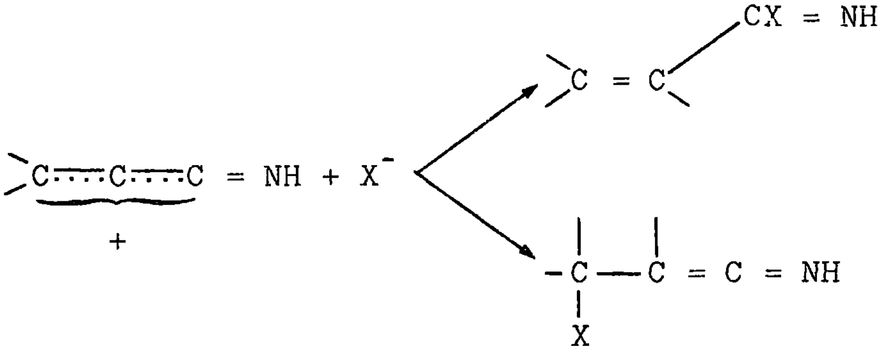


(5.22a)

(5.22b)

The nitrogen end is preferred since the positive charge is carried by the more electropositive carbon atoms and also the system can minimize the destabilizing effect of the positive charge in the presence of the π system.

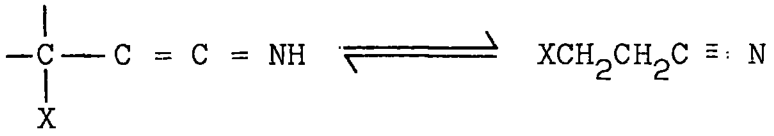
The second step is attack by the nucleophile at the carbon of the C=N or the terminal position of 5.22b (equation 5.23)



(5.23a)

(5.23b)

Only addition to the β carbon atom yields a stable produce, a tanimine. The ketenimine then undergoes tautomerism to the nitrile (equation 5.24).



$$-\underset{X}{\overset{|}{C}}-C=C=NH \rightleftharpoons XCH_2CH_2C\equiv N \qquad (5.24)$$

5.5 Conclusion

We have shown that the HCl and $SnCl_2$ in ether react as H^+ and $SnCl_3^-$ towards nitriles. It reacts with alkyl and aryl nitriles by addition across the C≡N triple bond and the intermediate dimerizes to an N(alkyl trichlorostannylmethylene) alkyl amidinium trichlorostannate II (Figure 5.1).

This has been proposed on the basis of the ratio of nitrile: Sn(total) : SnII of 2:2:1 implying a dimeric structure. This was further confirmed by the observation of two types of ethyl group in the ^1H nmr and the mass spectra which show fragments of the organic 'backbone' although no parent peaks. The nmr also shows unusual ^{14}N-H coupling. In contrast ACN undergoes addition across the C=C double bond to give β cyanoethyl tin trichloride which is considered dimeric in the solid and in non-coordinating solvents. Further work is in progress to confirm the salt structure by conductivity and to identify the hydrolysis products.

CHAPTER SIX

The Dimerization of Acrylonitrile by Cobalt Chloride and some electropositive metals

6.1 Introduction

The oligomerization of olefins, dienes and alkynes which can be produced in large quantities, is of considerable industrial importance since it affords routes to long chain polyfunctional intermediates. The dimerization of acrylic compounds is especially noteworthy since it yields bifunctional compounds, like adipates and glutarates, fundamental to the polymer industry in the production of condensation polymers such as nylon-6. The most common products from the dimerization of acrylonitrile are the straight chain dimers, *cis* and *trans* 1,4 dicyano butene(I), *cis* and *trans* dicyano butadiene(II), and dicyano butane III, and the branched chain dimer 1 methylene dicyanopropane IV (more commonly known as 2 methylene glutaronitrile).

Figure 6.1 Possible Dimers of Acrylonitrile

$NCCH{:}CHCH_2CH_2CN$

Ia

$NCCH_2CH{:}CHCH_2CN$

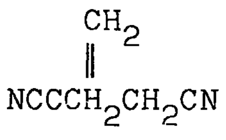
Ib

$NCCH{:}CH\text{-}CH{:}CHCN$

II

$NC(CH_2)_4CN$

III



$$NC\overset{\overset{CH_2}{\|}}{C}CH_2CH_2CN$$

IV

The most important of these are the straight chain dimers since they are precursors to adipic acid used in the production of 6,6 nylon.

Therefore the presently available methods of dimerization have been developed to produce soley straight chain dimers to the exclusion of any other oligomers. The methods of achieving this have been reviewed in Chapter One and the dimerization of acrylic compounds in general has been reviewed by Misono.[1] Therefore extensive discussion of the range of homogeneous catalytic dimerizations of acrylonitrile will not be repeated. Consideration of the published literature (Table 1.1) shows that most of the catalytic oligomerizations of ACN utilise expensive second and third row transition metal compounds. We were interested if any first row transition metal compounds could be effective in the preparation of linear dimers from acrylonitrile. The only published catalytic dimerizations of acrylonitrile by a first row transition metal are those effected by a metal halide such as $CoCl_2$ and a trialkylamine[2-6] or alkyl isocyanide[7] giving methylene glutaronitrile. However a report of the non catalytic dimerization of acrylonitrile yielding solely adiponitrile[8] according to equation 6.1 prompted us to investigate this reaction further.

$$CoCl_2 + ACN + Mn \xrightarrow{DMF} ? \xrightarrow[py]{H_2O} ADN \qquad (6.1)$$

In this chapter we have investigated the scope of the reaction for preparing dimers by varying the metal chloride, metal, solvent and olefin in order to optimize the reaction yields. We have also attempted to elucidate the mechanism of dimerization by a number of techniques in the hope that knowledge of the reaction mechanism might enable us to devise a reaction scheme to make the system catalytic. During the work several Japanese patents[9-13] were tested, which claimed that water need not be the source of hydrogen but that hydrogen gas at 100 atm. effects the formation of adiponitrile from the reaction mixture. We have been unable to repeat them.

6.2 Experimental

All the metal chlorides were dehydrated with thionyl chloride before use and all solvents were dried by standard techniques (see appendix A). Metal powders (Goodfellow or BDH) were used direct.

All reactions were carried out under standard anhydrous conditions. Reactions fell into two categories:

(1) those investigating a range of possible reagents using GLC for analysis; and

(2) those concerned with preparing samples of adiponitrile for detailed analysis.

The reactions in the first category were all carried out under the same conditions (i.e. room temperature with stirring for 24 hrs.) and the observations followed the same pattern: the $CoCl_2$ was added to ACN with or without solvent and the metal powder added with stirring. A successful reaction was usually indicated when the solution turned from blue, to dark green and then to red (DMF only).

Aliquots of hydrolysed sample were analysed by gas chromatography on a Pye Unicam GCD model fitted with a 3½% LAC on Embacel column at 160°C using nitrogen gas as a carrier. Samples for analysis were compared with authentic compounds.

Two typical reactions, one from each category, will be described in detail. Full results are summarized in Tables 6.1 a,b. In addition methyl acrylate and methyl methacrylate were substituted for acrylonitrile in the $CoCl_2$,Zn in dimethyl formamide system with no reaction and only $CoCl_2$ was found to be effective from the chlorides, $CoCl_2$, $MnCl_2$, $NiCl_2$, $SnCl_2$, $SnCl_4$.

6.2.1 The Reaction of Acrylonitrile with Cobalt Chloride and Manganese in dimethyl formamide

The reaction scheme outlined below is typical of the method used in assessing the scope of the reaction. $CoCl_2$ (5g) was dissolved in 50 ml. of dimethyl formamide and 5 ml. of acrylonitrile. 3.5g of manganese powder (<150 mesh) was added and the slurry stirred at room temperature. After 30 mins. the blue solution had turned green and a 5 ml. aliquot was removed. No adiponitrile (ADN) was detectable by GLC. The 5 ml. sample was added to 1 ml. of 50/50 pyridine: water mixture whereupon it turned pink and gave a brown precipitate. ADN could then be detected by GLC. No attempt was made to estimate the concentration. After 24 hrs. stirring the original reaction mixture had turned from green to brick red. No ADN was detectable but on hydrolysis with pyridine and water ADN was found as before.

6.2.2 The Reaction acrylonitrile with cobalt chloride and manganese metal

$CoCl_2$ (5g) was dissolved in 50 ml. of acrylonitrile. to this blue solution 3.5g of manganese powder was added with stirring. After ½ hr. the solution turned dark green and slowly deposited a green solid. To the green solution 25 ml. of water and 5 ml. of pyridine were added and the mixture warmed to $60^{\circ}C$ for 1 hr. The green solid and liquors gave a brown slurry in about 5 mins. The solid was separated by filtration leaving a pink solution which was discarded since GLC showed it to contain no adiponitrile.

The brown solid residue was worked up according to the method of Balard and Meybeck[14] for separating ACN oligomers. The solid was extracted in a Soxhlet apparatus with 100 ml.15/85 V/V dioxan/toluene mixture. The composition of the liquors was followed by thin layer chromatography using a silica stationary phase and a 15/85 V/V dioxan/toluene eluent. The plates were developed in iodine or viewed under a UV lamp, the former being more sensitive. After 48 hrs. extraction 4 components could be detected at Rf = 0.36, 0.46, 0.57 and 0.65. The major component (Rf=0.57) corresponded to ADN whilst the other components were identified as acrylamide (Rf=0.36) 1 methylene dicyanopropane (Rf=0.46) by comparison with authentic compounds and a trace of unknown compound (Rf=0.65), possibly silicone grease. The soxhlet liquors were concentrated and separated on a 30 cm. silica chromatography column using 15/85 V/V dioxan/toluene eluent. The eluent was collected in 10 ml. aliquots and analysed by TLC. Three fractions were detected and on removal of solvent from the combined fractions, containing ADN $\frac{1}{2}$ ml. of liquid was collected. The other two fractions yielded less than 10 μl. of sample and were discarded. The major component was studied by GLC, IR and NMR and shown to be identical with an authentic commercial sample of adiponitrile.

The brown residue from the soxhlet extraction was found to contain 48% carbon and was therefore washed with 50/50 V/V concentrated hydrochloric acid and dioxan to remove any inorganic material. The slurry was observed to vigorously liberate hydrogen from excess zinc metal yielding a dark green solution. 3g of an insoluble yellow residue was filtered off. Analysis gave it an empirical formula C_3H_3N and it was assumed to be polyacrylonitrile.

The reaction was repeated using deuterium oxide in place of water in the hydrolysis of the green intermediate to yield 1,4 dideutero adiponitrile.

6.2.3 Attempted Reactions

A. Attempted Isolation of Intermediate:

Attempts were made to isolate the green intermediate which, on hydrolysis, yields adiponitrile. The green compound precipitates irreverisbly from all solvents except DMF in which it decomposes to a red solution. In order to simplify any separation procedure the preferred solvent for reaction was acrylonitrile itself. The separation methods evolved were designed to separate unreacted metal powder, metal chloride, polyacrylonitrile, and intermediates. The insolubility of the precipitates precluded any simple solution based separation technique hence anhydrous column chromatography was attempted. Dry, neutral alumina and silica stationary phases were tried with solvents ranging in polarity from hexane through acetonitrile to dimethyl formamide. It was found that cobalt chloride was eluted by dioxan or acetonitrile on a silica column whilst it bound to an alumina column. The use of polar solvents such as dimethyl formamide or dimethyl sulphoxide were successful in the elution of the green compound but during elution the green material slowly turned brick red and adiponitrile was detected in the eluent indicating decomposition had occurred. No further attempts were made to isolate an intermediate.

B. Attempts to trap and observe reactive intermediates:

5 mg of the free radical trap, ^{t}BuNO[15,16], was added to the reaction of $CoCl_2$ with Zn and acrylonitrile in an attempt to isolate any free radicals generated so that they

might be studied by ESR. However no signals could be observed in any of the reaction mixtures although we were able to observe signals from a warmed solution of Bu^tNO and azoisobutrynonitrile in acrylonitrile, yet on addition of cobalt chloride to the solution the signals disappeared. It would seem that the paramagnetic cobalt ions cause considerable line broadening precluding the observation of any organic radicals.

C. High Pressure Reactions

The effect of hydrogen or carbon monoxide was studied at the Corporate Laboratory (Runcorn) of I.C.I. Ltd. in order to test Japanese claims that high pressure hydrogen yields adiponitrile directly in the reaction obviating the need to add water and also to attempt to insert carbon monoxide into any metal carbon bonds present.

A 100 ml. glass lined magnetically stirred autoclave was charged with 50 ml. of ACN or 5 ml. ACN in 50 ml. of DMF, 5g. $CoCl_2$ and 3g of Zn dust and pressurized to 100 atm with hydrogen or carbon monoxide. 1 ml. aliquots were withdrawn at 1 hr. intervals and tested by GLC for adiponitrile and other high boiling components on a 3½% LAC column at 180°C and for low boiling components on a 10% LAC column at 55°C. The aliquots were then hydrolysed by ½ ml. lf 50/50 V/V pyridine water mixture and the analysis repeated. In all systems no high boiling fractions and only a trace of propionitrile (Hydrogen filled autoclave only) were detected before hydrolysis up to 24 hrs. after starting the reaction. After hydrolysis adiponitrile was found in all systems together with trace amounts of propionitrile (Hydrogen filled autoclave only).

TABLE 6.1.a The Effect of Variation of Solvent on the Reaction of Acrylonitrile with Zn and $CoCl_2$

Solvent	Reaction[1]	Method of Analysis[2]
ACN	+	P, GLC
MeCN	+	GLC
DMF	+	P, GLC
DMSO	+	GLC
THF	?	GLC
EtOH	+	GLC
MeOH	+	GLC
Hexane	X	GLC
Toluene	X	GLC
H_2O	X	GLC

1. + = Reaction gives ADN according to analysis

X = Reaction gave no detectable ADN

2. P = ADN prepared from reaction, GLC = ADN detected by GLC and standard

TABLE 6.1.b Effect of Variation of Pure Metal on the Reaction of Cobalt Chloride and Metal in Acrylonitrile

Metal	Reaction[1]	Method of Analysis[1]
None	X	GLC
Mg	+	GLC
Zn	+	P, GLC
Mn	+	P, GLC
Fe	X	GLC
Ni	X	GLC
Cu	X	GLC

1. See Table 6.1.a.

6.3.1 Results and Discussion

The results of the experiments to investigate the scope of the reaction are given in Tables 6.1.a,b. Solvents of dielectric constant similar or greater than acetonitrile are satisfactory (namely solvents in which $CoCl_2$ is soluble) although the reaction proceeds only slowly in ethers and not at all in water. All the satisfactory solvents gave blue solutions of $CoCl_2$ indicating that tetrahedrally coordinate cobalt is present whereas the reaction does not proceed in water in which cobalt ions are octahedrally coordinate. Cobalt chloride is the only reactive metal chloride.

Electropositive metals affect the reaction, although it was observed that the most electropositive metal, Mg, caused reduction of cobalt chloride to cobalt metal in addition to forming the green 'adduct' at room temperature and manganese and zinc reduced $CoCl_2$ to the metal if the solutions were warmed to 50°C. The reaction appears to be dependent on the electropotential of the metal used. Metals equal or more electropositive than zinc ($Zn \longrightarrow Zn^{2+}(aq)$ $E^o = 0.76$ V, $Mn \longrightarrow Mn^{2+}(aq)$ $E^o = 1.05V$, $Mg \longrightarrow Mg^{2+}(aq)$ $E^o = 2.34V$) are effective whilst those equal or less electropositive than iron are not ($Fe \longrightarrow Fe^{2+}(aq)$ $E = 0.44V$, $Ni \longrightarrow Ni^{2+}(aq)$ $E^o = -0.23$, $Cu \longrightarrow Cu^{2+}(aq)$ $E^o = 0.34V$). No attempt has been made to determine the potential more precisely by chemical means since the reduction potentials are considerably solvent dependent and therefore aqueous reduction potentials may not hold in acrylonitrile.

Studies of the green intermediate were limited by the difficulties encountered in its separation from cobalt chloride, zinc metal, zinc chloride and polyacrylonitrile.

The proton decoupled ^{13}C nmr spectrum of dideuteroadiponitrile confirms that the deuteration occurs in symmetric positions (i.e. 1,4 or 2,3) and is greater than 95% since the triplet due to the CHD group is not appreciably distorted (Figure 6.3). If there were significant amounts of partially or undeuterated compound present then the centre line of the triplet could be enhanced relative to the outer pair of the triplet due to a contribution from a methylene group. In adiponitrile the carbon atoms in the 1 and 4 position come into resonance at higher field than the 2 and 3 position carbon atoms[18] due to the large magnetic anisotropy of the nitrile group[19] which causes shielding of atoms on the C-N axis (Figure 6.4).

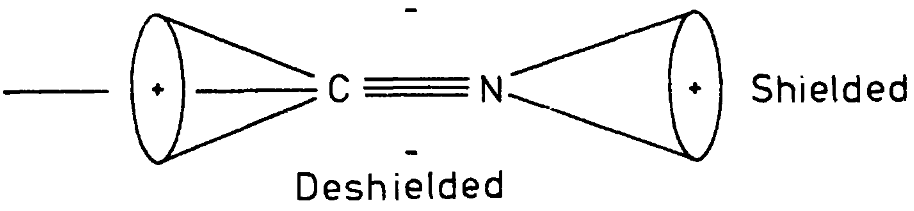


Figure 6.4

Therefore in dideuteroadiponitrile the absorptions at 26.98 ppm are assigned to the 2 and 3 positions whilst the CDH absorptions at 16.18 ppm are assigned to the 1 and 4 positions (Table 6.2). The ^{1}H nmr spectrum of dideuteroadiponitrile is consistent with this interpretation (Figure 6.5) with absorptions at 2.45 ppm and 1.83 ppm assigned to protons in the 1,4 and 2,3 positions respectively (Table 6.2).[20] The downfield shift of the 1,4 protons arises from the interaction

Figure 6.3 ^{13}C NMR Spectrum of d^2 Adiponitrile

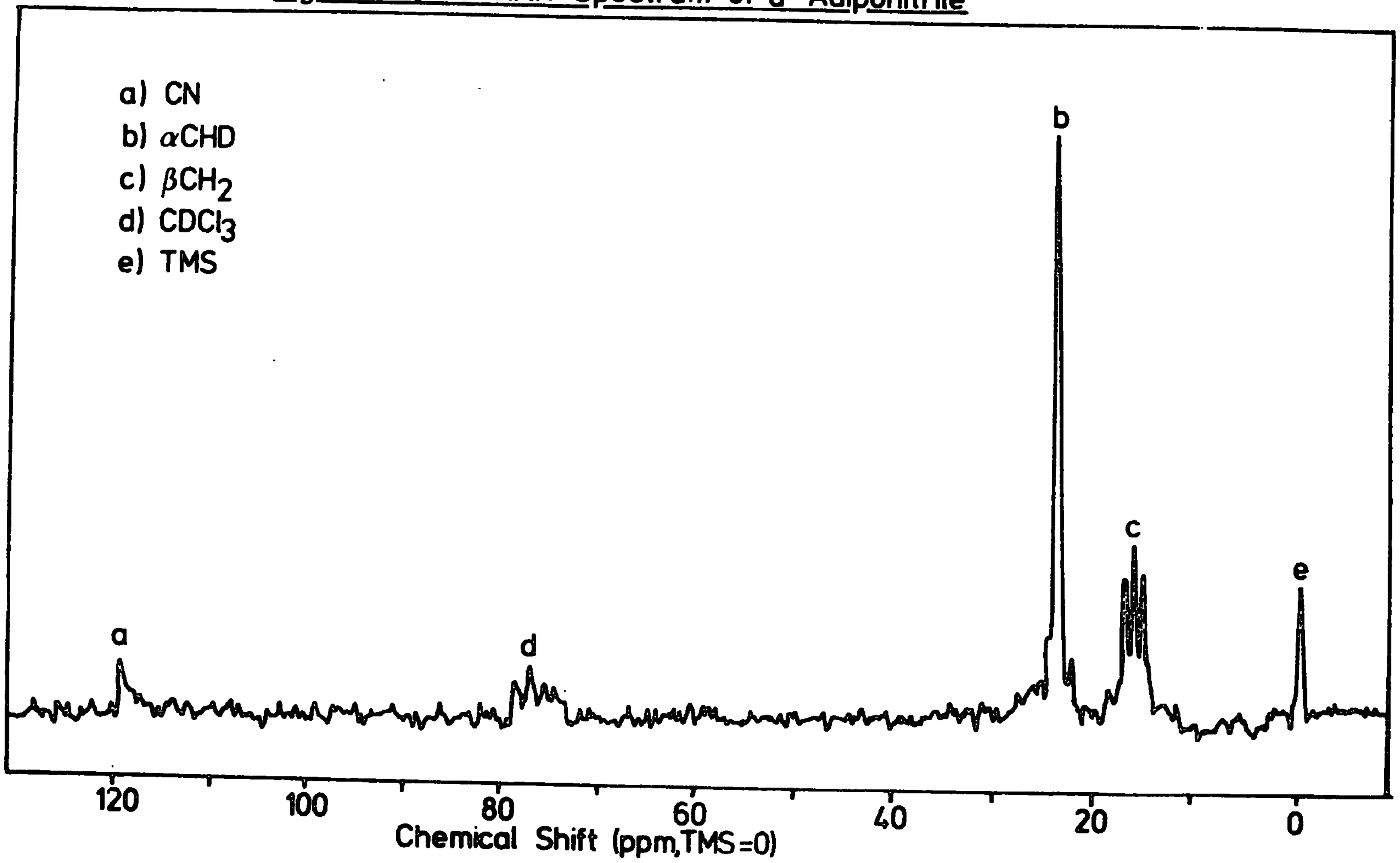
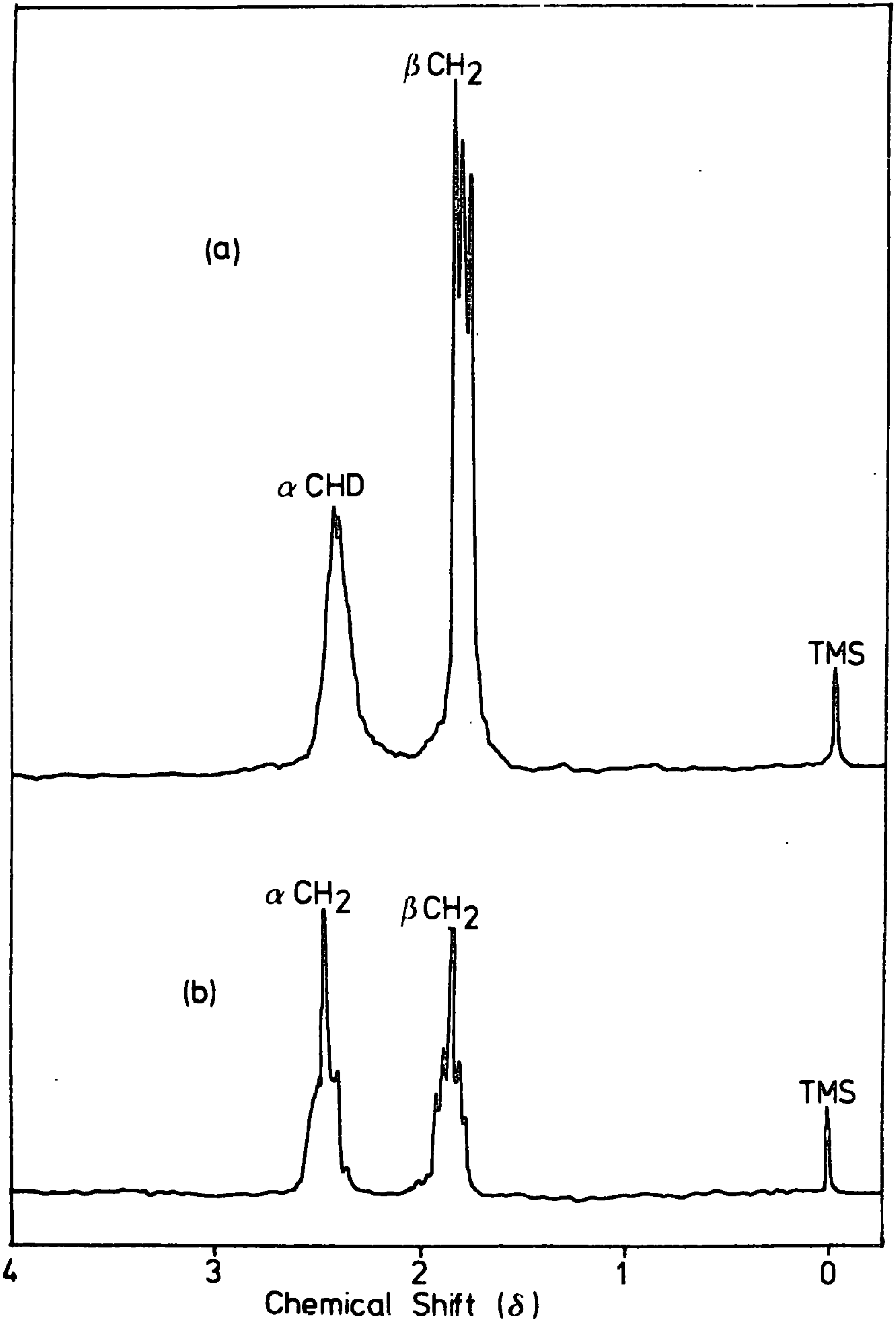


Figure 6.5, ^1H NMR Spectra of (a) d^2 ADN, (b) ADN



Hence no analytical data is reported and the discussion of spectroscopic data limited to general structural features.

The infra-red spectra of the green intermediates prepared by removal of solvent from the reaction of ACN, $CoCl_2$ and Mn or Zn showed several broad intense bands at 200-2300 cm^{-1} suggesting the presence of both coordinated and uncoordinated nitrile groups. Similarly weak absorptions in the region 1600-1650 imply the presence of an olefinic link. The mass spectrum of the same compound showed peaks due to the dimer fragments $C_6H_7N_2^+$ at M/e 107 (Figure 6.2.a) and $C_5H_7N^+$ at M/e 81 (Figure 6.2.b) but no higher mass fragments attributable to organo-metallic species

$N{\equiv}C - CH_2CH_2CH_2{}^+CHCN$

Figure 6.2.a

$NCCH_2CH_2CH_2{}^+CH$

Figure 6.2.b

Therefore we conclude that the green compound contains a straight chain acrylonitrile dimer.

Since the green intermediate is known not to contain free adiponitrile, the compound was hydrolysed with deuterum oxide so that information could be gained regarding the mode of bonding to the metallic substrate.

The mass spectrum of the deuteroadiponitrile shows a parent ion due to $d_2(ADN)^+H$ with a fragmentation pattern analogous to that of adiponitrile. A measurement of the percentage deuteration was attempted by comparing intensities of the peaks in the mass spectra of adiponitrile and dideuteroadiponitrile. However the relative intensities of the spectra were strongly pressure dependent due to ion-molecule reactions of the nitrile group[17] and comparable fragmentation intensities could not be obtained.

of the proton with the deshielding part of the magnetic field of the nitrile (Figure 6.4) rather than from an inductive electron withdrawal by an electronegative group.

The splitting of the pmr spectra is complex due to D-H and D-C-C-H coupling, and a detailed analysis of the

TABLE 6.2 90 MHz NMR Spectra of 1,4 dideuteroadiponitrile[1]

Nucleus	NC^*	$\overset{+}{C}DH$	$CH_2{}^{\dagger}$
^{13}C	118.84 br^3(1)	16.18t^2(J=45.2Hz)(1)	26.98(1)
^1H		2.45 br (1)	1.83 br (2)
^1H pure ADN		2.45t^2(J=6.25Hz)	1.83q (J=3.5Hz)(1)

(1) $NC^*\overset{+}{C}DH\,\overset{\dagger}{C}H_2\overset{\dagger}{C}H_2\overset{+}{C}DH\,\overset{*}{C}N$, Recorded in $CDCl_3$, Internal TMS(Oppm)

(2) d = doublet, t = triplet, q = quintet

(3) Assignment ref. 20

spectrum is outside of this discussion.

Finally we conclude from ^1H nmr and ^{13}C nmr that the product of deuterolysis of the green intermediate is 1,4 dideuteroadiponitrile.

6.3.2 High Pressure Reaction

A number of Japanese patents claim that, in addition to the dimerization of acrylonitrile by hydrolysis of the green intermediate,[9-13] adiponitrile may also be prepared by hydrogenation of the reaction mixture $CoCl_2$, Zn and ACN in DMF with hydrogen at 40 atmospheres pressure[9,10]. We were unable to repeat this reaction under the conditions stated in the patent and it may have been that the Japanese workers did not use totally anhydrous conditions leading to *in situ* hydrolysis of the intermediate to ADN.

6.3.3 Reaction Mechanism

The original workers[8] proposed that the green intermediate had a metal hydride structure shown in Figure 6.6.

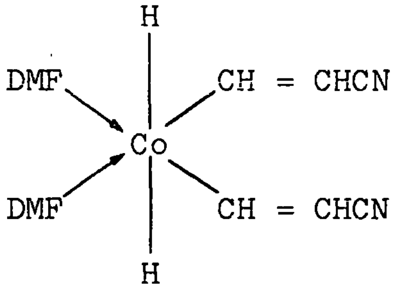
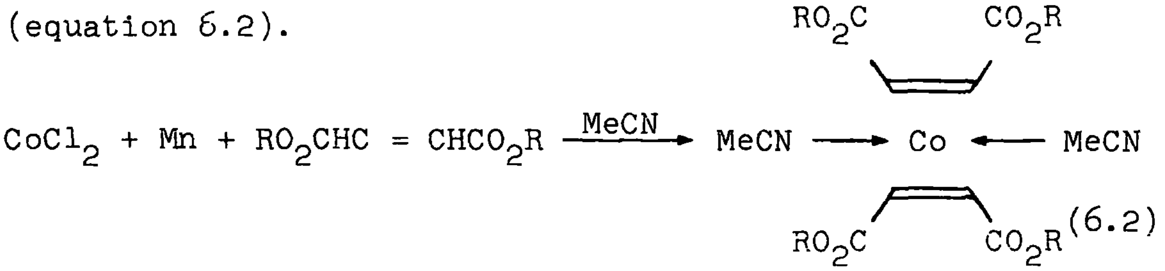


Figure 6.6

This structure seems implausible in view of our experiments since no M-H stretch is observed in the infra-red and we have observed dimeric fragments from the intermediate by mass spectroscopy. Also the structure would be expected to yield hydrogen on hydrolysis.

We will develop and discuss several plausible reaction mechanisms for the dimerization reaction since the mechanistic information available is limited by our inability to isolate and characterize a pure sample of the green intermediate.

The mechanism must be consistent with the observation of dimeric fragments in the mass spectrum and the intermediate must contain the dimer bonded by carbon in 1 and 4 positions of adiponitrile to the metal substrate as indicated by the deuterolysis experiments. The substrate metal is assumed to be cobalt in all cases since the reaction proceeds with a variety of electropositive elemental metals and cobalt chloride is the only effective metal chloride. Further evidence for this view comes from the reported preparation of bis-acetonitrile bis diethyl fumarate cobalt(o) from cobalt chloride, manganese metal and diethyl fumarate in acetonitrile[21] (equation 6.2).



$$CoCl_2 + Mn + RO_2CHC = CHCO_2R \xrightarrow{MeCN} MeCN \longrightarrow \underset{RO_2C\diagup\!=\!\diagdown CO_2R}{\overset{RO_2C\diagdown\!=\!\diagup CO_2R}{Co}} \longleftarrow MeCN \tag{6.2}$$

In this reaction the manganese metal is acting as a reducing agent for cobalt II and not reacting with the olefin. However acrylonitrile has been shown to react with electropositive metals by one electron transfer as in the dimerization of acrylonitrile to adiponitrile by sodium amalgam[1] (equation 6.3)

$$\begin{aligned} &ACN = Na/Hg \longrightarrow {}^{\bullet}CH_2\overline{C}HCN + Na^{+} \\ &HX + {}^{\bullet}CH_2\overline{C}HCN \longrightarrow {}^{\bullet}CH_2CH_2CN + X^{-} \\ &2\ {}^{\bullet}CH_2CH_2CN \longrightarrow NC(CH_2)_4CN \end{aligned} \tag{6.3}$$

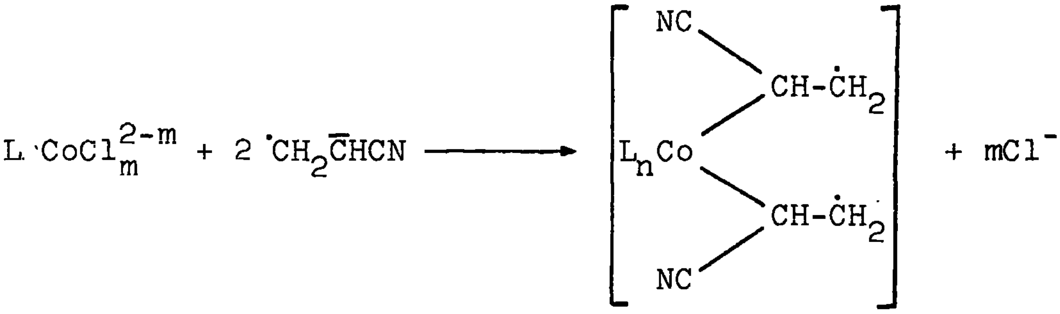
Hence we must consider two possible initial steps, the reduction of cobalt $\underline{\overline{0}}$ or I or the reduction of acrylonitrile by one electron transfer.

6.3.3.A A Reaction mechanism based on the reduction of acrylonitrile

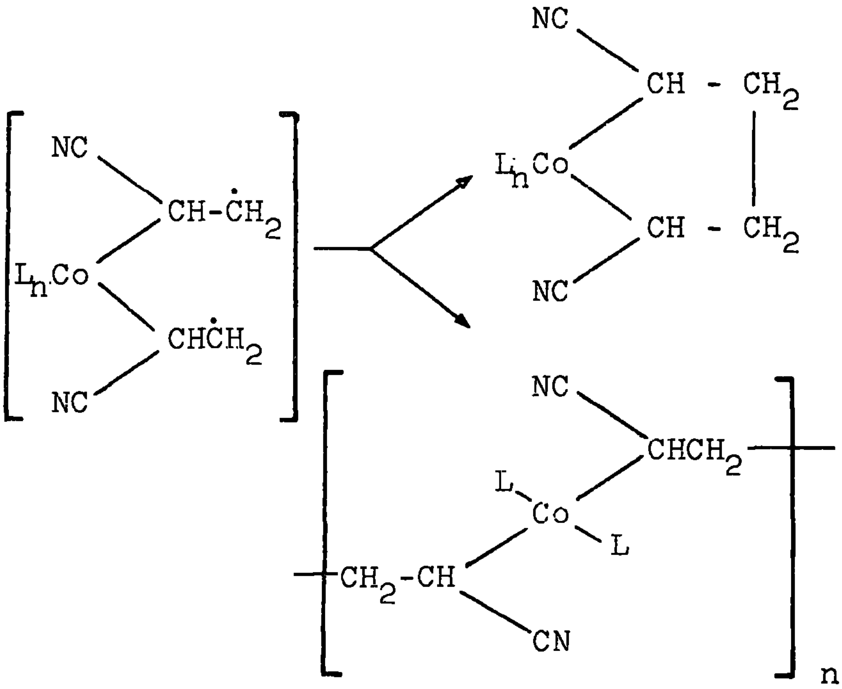
We will propose a reaction scheme based on the one electron transfer reduction of acrylonitrile. The electropositive metal transfers one electron to acrylonitrile analogously to the alkali metal dimerization to give a radical anion (equation 6.4)

$$M + 2CH_2 = CHCN \longrightarrow 2\ {}^{\bullet}CH_2\overline{C}HCN + M^{2+} \tag{6.4}$$

The radical anion then reacts with the cobalt chloride species in solution (see Chapter Two for a more detailed discussion of solute behaviour in acrylonitrile) eliminating chloride ion. The step is repeated to give an organocobalt diradical intermediate (equation 6.5) which reorganises to give the green intermediate, either a 5 membered metallocycle or a polymeric compound (equation 6.6) with interlinking organic groups. We favour the polymeric intermediate in view of the insolubility of the material and the difficulty of separation, although

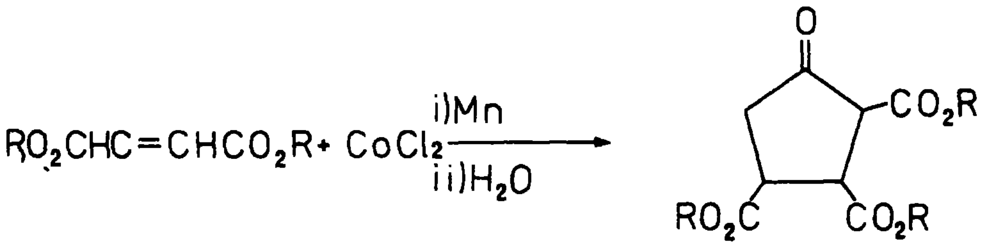


(6.5)



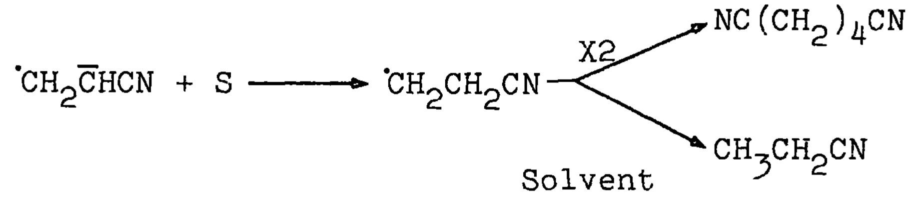
(6.6)

this reaction applied to dialkyl maleates yields trialkyl cyclopentanone 2,3,4 tricarboxylates.[22,23] This would be consistent with the elimination of a cobalt alkoxide from a metallocyclic intermediate (equation 6.7)



6.7

This reaction scheme is consistent with the mass spectrum of the intermediate and deuterolysis of such organocobalt compounds will yield 1,4 dideuteroadiponitrile. However the presence of free cyanoethyl radical anions would be expected to give rise to detectable quantities of adiponitrile and propionitrile prior to hydrolysis due to proton abstraction by the anion from the solvent (equation 6.8). No adiponitrile or propionitrile have been detected prior to hydrolysis.



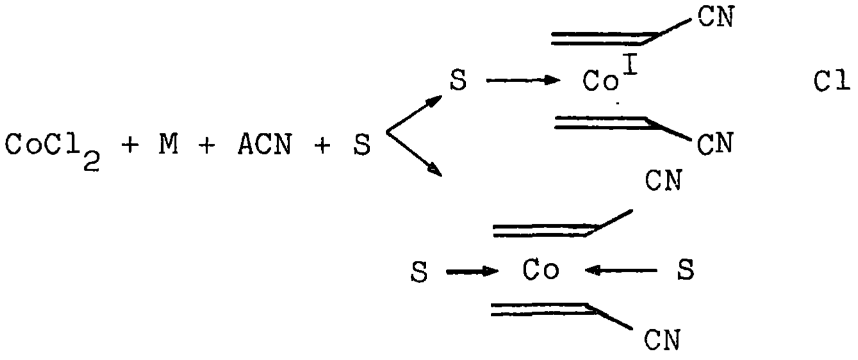
(6.8)

6.3.3.B. A Reaction Scheme based on the Reduction of Cobalt Chloride

The reduction of cobalt chloride by an electropositive metal such as manganese or zinc yield cobalt $\underline{0}$ complexes in the presence of diethyl fumarate[21] or halogenotris(triarylphosphine)cobalt I in the presence of a triarylphosphine[24] (although ACN is not dimerized by the latter[25]).

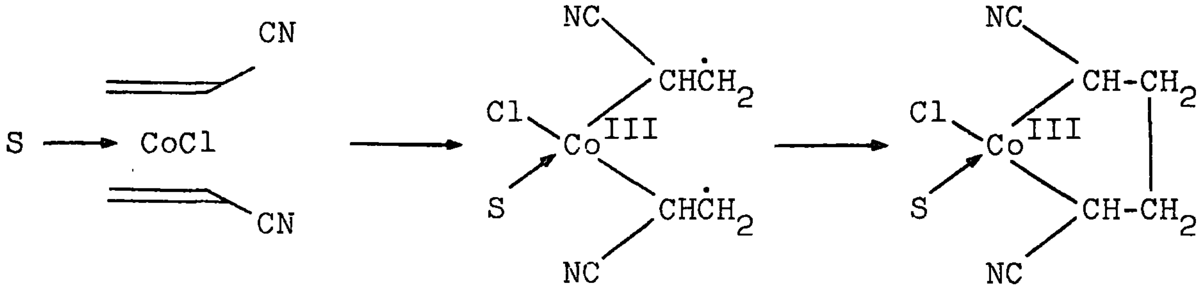
Hence we propose an initial step involving the reduction of cobalt chloride. The extent of reduction is unknown at present and therefore two, closely related, reaction pathways can be considered, one with cobalt in the zerovalent state and one with cobalt I as the reactive species.

Reduction of cobalt chloride may yield an intermediate π complex by analogy with equation 6.2 (equation 6.9).

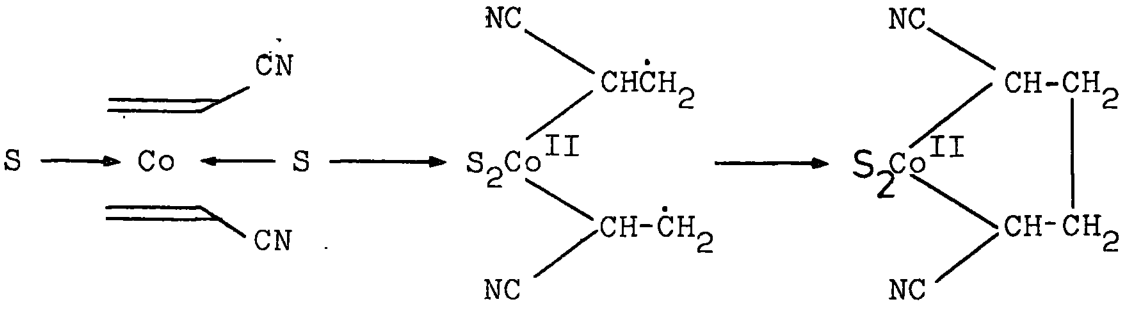


(6.9)

The π complexes then undergo oxidative addition of two molecules of acrylonitrile followed by cyclization to a 5-membered metallocycle or polymer as in equation 6.6 (equation 6.10 a,b).



or polymeric species (6.10a)

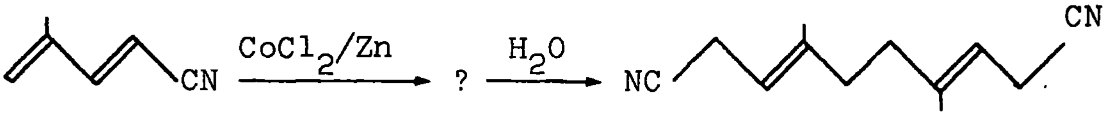


or polymeric species (6.10b)

The major difference between the two routes is in the oxidation state of the cobalt metal. This question is arriverable in principle by accurate measurement of the yield of adiponitrile and the quantity of metal consumed. However the separation difficulties described in the experimental section 6.2 preclude this. We propose instead to explore the reaction of some well characterized cobalt $\underline{\overline{0}}$ or I olefin complexes with acrylonitrile.

6.3.3.C A reaction scheme based on the nitrile group

Cobalt chloride and zinc metal are known to dimerize 4 methyl 2,4 pentadienenitriles to 4,7 dimethyl 3,7 decadienedinitrile[26] (equation 6.11).*



We have shown that acrylic esters are unaffected by the reaction mixture. Therefore it appears that this reaction is unique to terminally unsaturated nitriles. The following scheme attempts to take some account of this uniqueness by invoking a reaction intermediate bonded to the nitrile group.

The insertion of an alkene into a metal carbon bond is well established[27] and the reaction is usually highly stereospecific as in Ziegler-Natta catalysed olefin polymerization. Such an insertion reaction in the dimerization reaction not only obviates the need to postulate free radical intermediates but also accounts for the formation of soley adiponitrile.

We suggest that the reduced cobalt solvate or π complex (CoX_n where X = solvent and/or ACN) undergoes rearrangement to a σ alkyl species (equation 6.12a) with the

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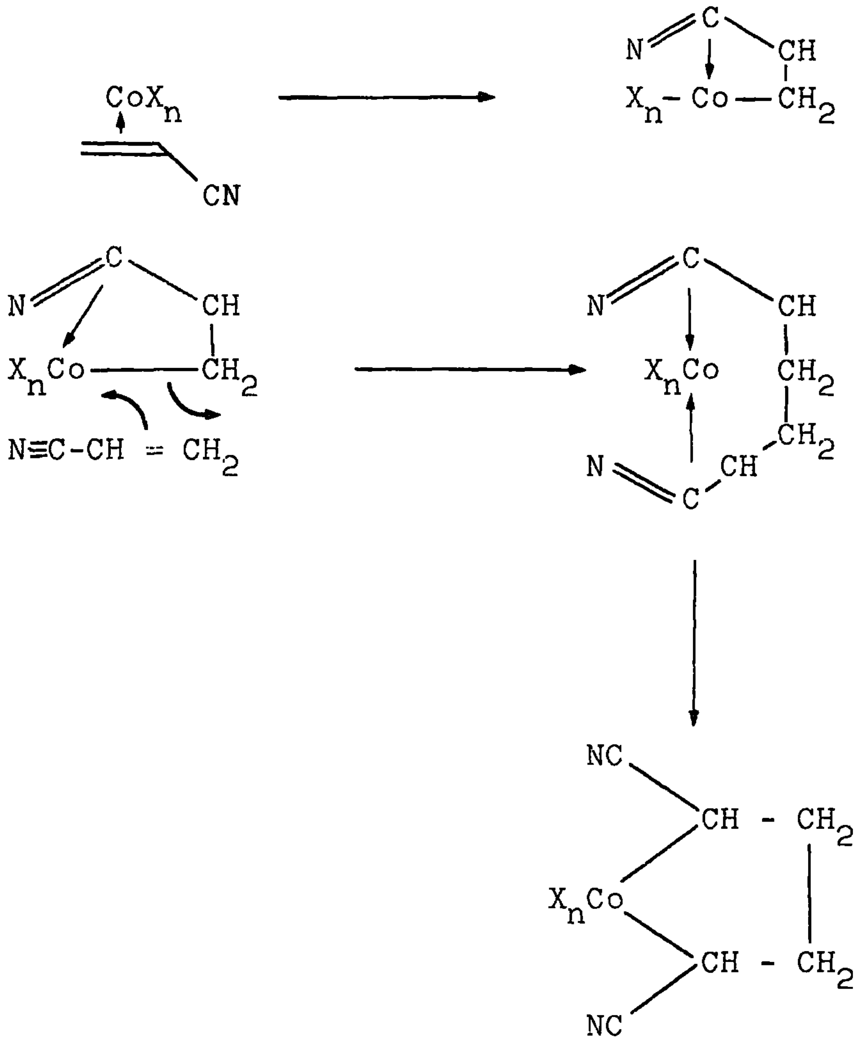
* Erroneously referred to as 4,8 dimethyl 3,7 decadienedinitrile in Ref. 26.

nitrile group bonded as a pseudo alkyl group. A further molecule of acrylonitrile then undergoes insertion into the cobalt-carbon bond to give a pseudo *bis* allyl which may rearrange to give a σ bonded metallocycle (equation 6.11.b).



(6.12a)

This reaction scheme is applicable to any α, β unsaturated nitriles, such as the dimerization of pentadienenitriles in equation 6.11 whilst α, β unsaturated esters form only the π adduct (equation 6.2).

6.4 Conclusion

We have shown that the dimerization reaction discovered by Agnes[8] is unique to nitriles and that the dimerization may be effected by a wide range of electropositive metals in solvents which dissolve cobalt chloride. The mechanism of the reaction has been shown to include a 1,4 metallosubstituted adiponitrile derivative which yields 1,4 dideuteroadiponitrile on deuterolysis. Several different mechanisms have been discussed, the mechanism proposed by the original workers being found inadequate.

The evidence favours a mechanism which accounts for the uniqueness of the reaction towards nitriles and also its high stereospecificity. We consider that scheme 6.3.3.C most closely fits the available information.

Further work is in progress, preparing some olefin cobalt $\overline{\underline{0}}$ complexes for direct reaction with acrylonitrile.

APPENDIX A

Analytical Methods

1. Element Analyses:

Carbon, Hydrogen and Nitrogen were determined using a Perkin-Elmer 240 Elemental Analyser. Samples were sealed into preweighed aluminium capsules in a glove box. Nitrogen was also determined by the Kjeldhal method. Chlorine was determined by oxygen flask combustion followed by potentiometric titration of the chloride ions. Metals except for tin were analysed by oxygen flask combustion followed by Atomic Absorption spectrophotometry.

Analyses for SnII was performed according to a modified method of Vogel. The method depends on the oxidation of tin II to tin IV by iodine in the presence of a high concentration of hydrochloric acid.

$$Sn^{2+} + I_2 \text{ —— } Sn^{4+} + 2I^-$$

The titration was conducted under a nitrogen atmosphere to prevent aerial oxidation of tin II to tin IV. Water and concentrated HCl used for solutions were degassed with a stream of nitrogen. The procedure adopted was as follows. 200-500mg of compound were weighed out in a glove box. This was dissolved in 150ml of concentrated HCl, transferred to a 250ml flask and made up to 250ml by degassed water. 50ml of solution was transferred to a flask continuously purged with nitrogen via a side arm and diluted with 50ml of degassed water. The solution was titrated with 0.05m iodine solution, using 2ml of starch as indicator, to the first appearance of a blue colour. The procedure was repeated with 2 further aliquots.

The percentage of tin was found from 1ml.$I_2 \equiv 0.11870$g of SnII. Titrations were typically 5-10ml and end point reproducibility was ± 0.05ml. Tin analyses were not attempted on most tin IV compounds since they contained covalently bonded tin-halogen species. This rendered the compounds volatile and loss of sample was experienced during decomposition to oxide for gravimetric analysis or reduction to tin II by boiling with lead powder and concentrated hydrochloric acid as recommended by Vogel.

2. Spectroscopic Analysis:

Infra-red spectra were recorded on Perkin-Elmer 477 and 577 spectrometers in the range 4000-250 cm^{-1} and 4000-200 cm^{-1} respectively. Liquid samples and solid samples as nujol mulls were pressed between KBs or Csl plates depending on the region to be studied.

'H NMR spectra were recorded on a continuous wave Varian A60/56D spectrometer operating at 60MHz and also a fourier transform Bruker HX90E spectrometer operating at 90MHz. ^{13}C NMR spectra were recorded using the same Bruker machine operating at 22,6350 MHz.

The mass spectra of solid compounds were measured on an AEI MS9 mass spectrometer using electromagnetic scanning, an accelerating voltage of 70eV and a probe temperature of 180-200°C. The spectra of liquids were measured by direct injection into a V.G. Micromass 12B spectrometer. The spectra were recorded using conventional UV chart recorder or later a V.G. Datasystem 2000 which enabled automatic counting and plotting of the spectra by means of a PDP8/3a minicomputer, a Descope visual display unit and a Bryans X-Y plotter.

The glove box atmosphere was maintained by continuous purge whilst the box was in use and continuous recycling through a KOH tower, a heated copper tower and a P_2O_5 tower to remove acid gases, oxygen and water respectively. All external tubing was of nylon or glass with joints sealed with silicone rubber.

3. Starting materials:

(a) Metal chlorides.

Involatile metal chlorides, $NiCl_2$, $CoCl_2$, $MnCl_2$ and $ZnCl_2$ were prepared by dehydrating commercial hydrated samples by refluxing with freshly distilled thionyl chloride for 24 hrs. The thionyl chloride was then distilled to dryness and the metal chloride pumped at 0.01 torr for 6-7 hrs. at 100°C to remove final traces of thionyl chloride.

Anhydrous zinc chloride was also prepared by dissolving zinc metal in ether saturated with hydrogen chloride. Excess zinc was removed on a grade 4 frit and the ether removed by pumping for 12 hrs. to leave anhydrous zinc chloride (99% + on zinc). Volatile metal chlorides, $SbCl_5$, $SnCl_4$, $TiCl_4$, $GeCl_4$ and $SiCl_4$ were vacuum distilled before use.

(b) Solvents.

Acrylonitrile was purified by stirring with calcium hydride (10g/l) for 6 hrs. and distilling into fresh calcium hydride to remove water and stabilizer (hydroquinone). The distilled ACN was refluxed for a further 6 hrs. and fractionally distilled using a Vigreux column onto freshly activated 3A molecular sieve, discarding the first and last 15% of distillate. The ACN was stored in flasks enclosed in plastic bags to prevent UV initiated polymerization in the absence of stabilizer.

Acetonitrile was repeatedly distilled from P_2O_5 until no colour change in the P_2O_5 occurred and stored over 3A molecular sieve.

Dimethyl formamide and dimethyl sulphoxide were purified by preliminary drying with dry magnesium sulphate followed by shaking with KOH for 5 mins. The decanted solvent was distilled from anhydrous alumina at 15-20 torr up a 40cm Vigreux column and the 15-85% cut stored over freshly activated molecular sieve.

Tetrahydrofuran was dried by refluxing with potassium metal. Diethyl ether, dioxan, toluene and other hydrocarbon solvents were dried with sodium wire.

APPENDIX C

The Board of Studies in Chemistry requires that each postgraduate research thesis should contain an appendix listing all research colloquia, seminars and lectures (by external speakers) arranged by the Department of Chemistry during the period when research for the thesis was carried out.

Research Colloquia, Seminars and Lectures Arranged by the Department of Chemistry between October 1976 and September 1979

20 October 1976

Professor J.B. Hyne (University of Calgary), "New Research on an Old Element - Sulphur"

10 November 1976

Dr. J.S. Ogden (University of Southampton), "The Characterisation of High Temperature Species by Matrix Isolation"

17 November 1976

Dr. B.E.F. Fender (University of Oxford), "Familiar but Remarkable Inorganic Solids"

24 November 1976

Dr. M.I. Page, (Huddersfield Polytechnic), "Large and Small Rate Enhancements of Intramolecular Catalysed Reactions"

8 December 1976

Professor A.J. Leadbetter (University of Exeter), "Liquid Crystals"

26 January 1977

Dr. A. Davis (E.R.D.R.), "The Weathering of Polymeric Materials"

2 February 1977

Dr. M. Falk, (N.R.C. Canada), "Structural Deducations from the Vibrational Spectrum of Water in Condensed Phases"

9 February 1977

Professor R.O.C. Norman (University of York), "Radical Cations; Intermediates in Organic Reactions"

23 February 1977

Dr. G. Harris (University of St. Andrews), "Halogen Adducts of Phosphines and Arsines"

25 February 1977

Professor H.T. Dieck (Frankfurt University), "Diazadienes - New Powerful Low-Valent Metal Ligands"

2 March 1977

Dr. F. Hibbert (Birkbeck College, University of London), "Fast Reaction Studies of Slow Proton Transfers Involving Nitrogen and Oxygen Acids"

4 March 1977

Dr. G. Brink (Rhoes University, South Africa), "Dielectric Studies of Hydrogen Bonding in Alcohols"

9 March 1977

Dr. I.O. Sutherland (University of Sheffield), "The Stevans' Rearrangement: Orbital Symmetry and Radical Pairs"

18 March 1977

Professor H. Bock (Frankfurt University), "Photoelectron Spectra and Molecular Properties: A Vademecum for the Chemist"

30 March 1977

Dr. J.R. MacCallum (University of St. Andrews), "Photooxidation of Polymers"

20 April 1977

Dr. D.M.J. Lilley (Research Division, G.D. Searle), "Tails of Chromatin Structure - Progress Towards a Working Model"

27 April 1977

Dr. M.P. Stevens (University of Hartford), "Photocycloaddition Polymerisation"

4 May 1977

Dr. G.C. Tabisz (University of Manitoba), "Collison Induced Light Scattering by Compressed Molecular Gases"

11 May 1977

Dr. R.E. Banks (U.M.I.S.T.), "The Reactions of Hexafluoropropene with Heterocyclic N-Oxides"

18 May 1977

Dr. J. Atwood (University of Alabama), "Novel Solution Behaviour of Anionic Organoaluminium Compounds: the Formation of Liquid Clathrates"

25 May 1977

Professor M.M. Kreevoy (University of Minnesota), "The Dynamics of Proton Transfer in Solution"

1 June 1977

Dr. J. McCleverty (University of Sheffield), "Consequences of Deprivation and Overcrowding on the Chemistry of Molybdenum and Tungsten"

6 July 1977

Professor J. Passmore (University of New Brunswick, Canada), "Adducts Between Group V Pentahalides and a Postscript on S_7I^+"

27 September 1977

Dr. T.J. Broxton (La Trobe University, Australia), "Interaction of Aryldiazonium Salts and Arylazoalkyl Ethers in Basic Alcoholic Solvents"

19 October 1977

Dr. B. Heyn (University of Jena, D.D.R.), "σ-Organo-Molybdenum Complexes as Alkene Polymerisation Catalysts"

27 October 1977

Professor R.A. Filler (Illinois Institute of Technology), "Reactions of Organic Compounds with Xenon Fluorides"

2 November 1977

Dr. N. Boden (University of Leeds), "N.M.R. Spin-Echo Experiments for Studying Structure and Dynamical Properties of Materials Containing Interacting Spin-$\frac{1}{2}$ Pairs"

9 November 1977

Dr. P.A. Madden (University of Cambridge), "Raman Studies of Molecular Motions in Liquids"

14 December 1977

Dr. R.O. Gould (University of Edinburgh), "Crystallography to the Rescue in Ruthenium Chemistry"

25 January 1978

Dr. G. Richards (University of Oxford), "Quantum Pharmacology"

1 February 1978

Professor K.J. Ivin (Queens University, Belfast), "The Olefin Metathesis Reaction: Mechanism of Ring-Opening Polymerisation of Cycloalkenes"

<u>3 February 1978</u>

Dr. A. Hartog (Free University, Amsterdam), "Some Surprising Recent Developments in Organo-Magnesium Chemistry"

<u>22 February 1978</u>

Professor J.D. Birchall (Mond Division, I.C.I. Ltd.), "Silicon in the Biosphere"

<u>1 March 1978</u>

Dr. A. Williams (University of Kent), "Acyl Group Transfer Reactions"

<u>3 March 1978</u>

Dr. G. van Koten (University of Amsterdam), "Structure and Reactivity of Arylcopper Cluster Compounds"

<u>15 March 1978</u>

Professor G. Scott (University of Aston), "Fashioning Plastics to Match the Environment"

<u>22 March 1978</u>

Professor H. Vahrenkamp (University of Freiburg), "Metal-Metal Bonds in Organometallic Complexes"

<u>19 April 1978</u>

Dr. M. Barber (U.M.I.S.T.), "Secondary Ion Mass Spectra of Surfaces Adsorbed Species"

<u>15 May 1978</u>

Dr. M.I. Bruce (University of Adelaide), "New Reactions of Ruthenium Compounds with Alkynes"

<u>16 May 1978</u>

Dr. P. Ferguson (C.N.R.S., Grenoble), "Surface Plasma Waves and Adsorbed Species on Metals"

18 May 1978

Professor M. Gordon (University of Essex), "Three Critical Points in Polymer Science"

22 May 1978

Professor D. Tuck (University of Windsor, Ontario), "Electrochemical Synthesis of Inorganic and Organometallic Compounds"

24/25 May 1978

Professor P. von R. Schleyer (University of Erlangen, Nurnberg),

(i) "Planar Tetra-Coordinate Methanes, Perpendicular Ethylenes and Planar Allenes"
(ii) "Aromaticity in Three Dimensions"
(iii) "Non-Classical Carbocations"

21 June 1978

Dr. S.K. Tyrlik (Academy of Sciences, Warsaw), "Dimethylglyoxime-Cobalt Complexes - Catalytic Black Boxes"

23 June 1978

Professor W.B. Person (University of Florida), "Diode Laser Spectroscopy at 16 μm"

27 June 1978

Professor R.B. King (University of Georgia, Athens, Georgia, U.S.A.), "The Use of Carbonyl Anions in the Synthesis of Organometallic Compounds"

30 June 1978

Professor G. Mateescu (Cape Western Reserve University), "A Concerted Spectroscopy Approach to the Characterisation of Ions and Ion Pairs: Facts, Plans and Dreams"

15 September 1978

Professor W. Siebert (University of Marburg, West Germany), "Boron Heterocycles as Ligands in Transition Metal Chemistry"

22 September 1978

Professor T. Fehlner (University of Notre Dame, U.S.A.), "Ferraboranes: Syntheses and Photochemistry"

12 December 1978

Professor C.J.M. Stirling (University of Bangor), "Parting is Such Sweet Sorrow - the Leaving Group in Organic Reactions"

14 February 1979

Professor B. Dunnell (University of British Columbia), "The Application of N.M.R. to the Study of Motions in Molecules"

16 February 1979

Dr. J. Tomkinson (Institute Laue-Langevin, Grenoble), "Studies of Adsorbed Species"

14 March 1979

Dr. J.C. Walton (University of St. Andrews), Pentadienyl Radicals"

28 March 1979

Dr. A. Reiser (Kodak Ltd.), "Polymer Photography and the Mechanism of Cross-link Formation in Solid Polymer Matrices"

5 April 1979

Dr. S. Larsson (University of Uppsala), "Some Aspects of Photoionisation Phenomena in Inorganic Systems"

25 April 1979

Dr. C.R. Patrick (University of Birmingham), "Chlorofluorocarbons and Stratospheric Ozone: An Appraisal of the Environmental Problem"

1 May 1979

Dr. G. Wyman (European Research Office, U.S. Army), "Excited State Chemistry in Indigoid Dyes"

2 May 1979

Dr. J.D. Hobson (University of Birmingham), "Nitrogen-centred Reactive Intermediates"

8 May 1979

Professor A. Schmidpeter (Institute of Inorganic Chemistry, University of Munich), "Five-membered Phosphorus Heterocycles Containing Dicoordinate Phosphorus"

9 May 1979

Dr. A.J. Kirby (University of Cambridge), "Structure and Reactivity in Intramolecular and Enzymic Catalysis"

9 May 1979

Professor G. Maier (Lahn-Giessen), "Tetra-tert-butyltetrahedrane"

10 May 1979

Professor G. Allen, F.R.S. (Science Research Council), "Neutron Scattering Studies of Polymers"

16 May 1979

Dr. J.F. Nixon (University of Sussex), "Spectroscopic Studies on Phosphines and their Coordination Complexes"

23 May 1979

Dr. B. Wakefield (University of Salford), "Electron Transfer in Reactions of Metals and Organometallic Compounds with Polychloropyridine Derivatives"

13 June 1979

Dr. G. Heath, (University of Edinburgh), "Putting electrochemistry into mothballs - (Redox processes of metal porphyrins and phthalocynanines)".

14 June 1979

Professor I. Ugi (University of Munich), "Synthetic Uses of Super Nucleophiles"

20 June 1979

Professor J.D. Corbett (Iowa State University, Ames, Iowa, U.S.A.), "Zintl Ions: Synthesis and Structure of Homopolyatomic Anions of the Post-Transition Elements"

27 June 1979

Dr. H. Fuess (University of Frankfurt), "Study of Electron Distribution in Crystalline Solids by X-ray and Neutron Diffraction"

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