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THE COORDINATION CHEMISTRY OF ACRYLONITRILE

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A. INTRODUCTION

The aim of this review is to provide a lead into the extensive literature on the coordination chemistry of acrylonitrile, CH_2CHCN (also known as vinyl cyanide, cyanoethene or 2-propenenitrile). This compound has attracted considerable interest as a Lewis base because it possesses two functional groups, the cyano group $C{\equiv}N$ and the alkene link $C{=}C$, through either or both of which it can coordinate. As these represent typical hard and soft Lewis base functions, respectively, acrylonitrile can coordinate effectively with a wide range of Lewis acids. It is also an important industrial chemical, many of whose reactions involve coordinative interactions with Lewis acids as their first steps. This review is therefore concerned not only with systems in which acrylonitrile adducts have been isolated, but also with studies that have revealed or indicated weak coordinative interactions between acrylonitrile and various Lewis acids.

The table at the end of this review (Table 5) lists the systems that have been tested for Lewis acidity towards acrylonitrile, indicates the stoichiometry of adducts isolated, and shows whether the structures, spectra, reactivities or other properties of these adducts were studied. The reader interested in a specific system is advised to use this table as a direct lead into the literature (covered to mid-1981), as there is not enough space to discuss all of these systems in the text. Instead, we focus attention on a number of studies that we consider to illustrate the main features of acrylonitrile coordination chemistry. In this we have had to be subjective, and have paid particular attention to structural and spectroscopic studies that have revealed the mode by which acrylonitrile was coordinated (through its nitrile function, through its alkene function, or through both) and to the manner in which coordination modifies the properties and reactions of acrylonitrile.

The general chemistry of acrylonitrile was the subject of a book published in 1959 [1]. Since then, interest in its coordination chemistry, in common with other aspects of its chemistry, has developed very markedly. No comprehensive survey concerned exclusively with acrylonitrile coordination complexes has to our knowledge been published prior to the present review, although a few acrylonitrile adducts have received brief mention in surveys concerned with nitrile adducts in general [2,3] in surveys of transition metal–olefin complexes [4–6], and in reviews of more specific topics, e.g. nickel [7], palladium [8] and platinum [8] complexes, and adducts with

Group IV Lewis acids [9,10]. Some specific reactions of acrylonitrile that proceed via coordination complexes are discussed in refs. 11–14.

B. STRUCTURES OF ACRYLONITRILE ADDUCTS

(i) The structure and possible modes of coordination of acrylonitrile

In view of the potential versatility of acrylonitrile as a ligand, it is surprising that few definitive structural studies on its adducts have been carried out. For example, before our own work [15] on the nickel(II) complex $[Ni(NCCHCH_2)_6]^{2+}[Zn_2Cl_6]^{2-}$, no adduct in which acrylonitrile coordinates solely through its nitrile nitrogen atom had been the subject of an X-ray crystallographic study, though the structure of an N-bonded methacrylonitrile complex ($CuBr \cdot NCCMeCH_2$ [16]) had been determined, and infrared spectroscopic studies have shown this mode of coordination for acrylonitrile to be common.

Acrylonitrile itself has the planar structure shown in Fig. 1, which gives the bond distances and angles determined by a microwave spectroscopic study [17]. It can coordinate in three known ways, which we shall refer to as types (a), (b) and (c). Type (a) coordination (Fig. 2a), the preferred mode of coordination to a hard Lewis acid, is monohapto through the nitrogen 'lone pair' of its nitrile group. Type (b) coordination (Fig. 2b), the preferred mode

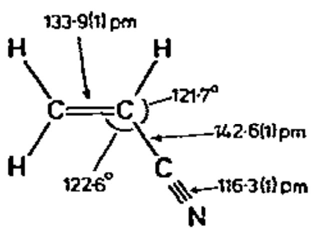


Fig. 1. Structure of uncoordinated acrylonitrile.

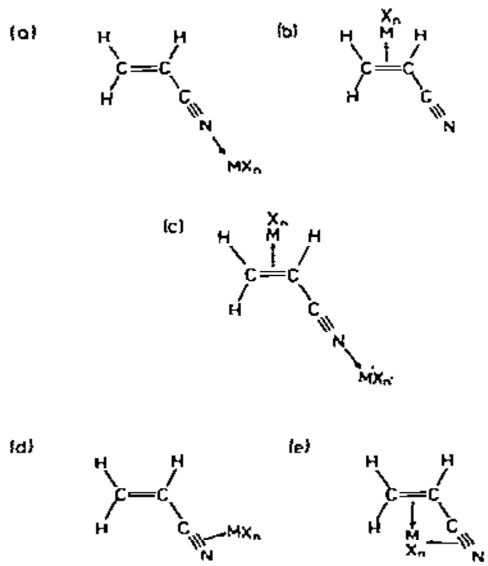


Fig. 2. Possible modes of coordination of acrylonitrile.

of coordination to a soft Lewis acid, is dihapto through its vinyl group. Type (c) coordination involves simultaneous coordination of both the above types when acrylonitrile acts as a bridge between two metal atoms (Fig. 2c).

Two other modes of coordination that are in principle possible for acrylonitrile are also illustrated in Fig. 2. These are dihapto-coordination through the nitrile group (Fig. 2d), and tetrahapto-coordination by simultaneous π-complex formation by both the vinyl group and nitrile group (Fig. 2e). No examples of these have yet been found. That they are unlikely can be seen from a consideration of the contributions made by individual atomic orbitals to the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals of acrylonitrile [18]. Both the HOMO and LUMO are π molecular orbitals arising from combinations of carbon and nitrogen p atomic orbitals (AO) orientated perpendicular to the plane of the molecule. Figure 3 shows the coefficients involved. They indicate that the HOMO is bonding with respect to both the alkene C=C and nitrile C≡N π-system, whereas the LUMO is both C=C and C≡N antibonding (in character, these two orbitals resemble the HOMO and LUMO of 1,3-butadiene). The coefficients also show that the contributions of the alkene p AO's are greater than those of the nitrile p AO's, so making the vinyl group the more likely site for π-complex formation because it affords better overlap of the orbitals needed both for donation of electronic charge from the HOMO to a suitable metal AO, and for back coordination from a filled metal AO to the LUMO. Dihapto coordination by acrylonitrile through its nitrile function alone (Fig. 2d) is thus exceedingly unlikely. Tetrahapto coordination through both the vinyl and nitrile functions (Fig. 2e) remains a remote possibility, though unlikely both for the above electronic reasons and for steric reasons—the C=C and C≡N units of acrylonitrile are less suitably orientated than are the two C=C units of a good tetrahapto ligand like *cis* 1,3-butadiene for simultaneous coordination to a common acceptor atom.

The structures of some acrylonitrile adducts that have been determined by

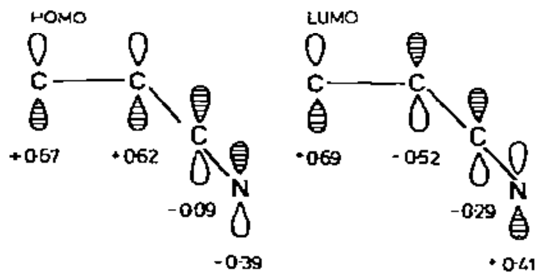


Fig. 3. Frontier orbitals of acrylonitrile, showing the coefficients of the p atomic orbitals involved.

X-ray crystallographic studies, and that illustrate coordination of types (a), (b) and (c), are discussed in the following sections.

(ii) Type (a) complexes, bonded through the nitrile nitrogen: the nickel complex $[Ni(NCCHCH_2)_6]^{2+}[Zn_2Cl_6]^{2-}$ and the methacrylonitrile complex $CuBr \cdot NCCMeCH_2$

Although there is ample spectroscopic evidence, as will be outlined in Section C, that many acrylonitrile complexes contain monohapto-, N-bonded nitrile ligands, only one such complex has, to our knowledge, been the subject of an X-ray crystallographic study. This is the nickel(II) complex $[Ni(NCCHCH_2)_6]^{2+}[Zn_2Cl_6]^{2-}$, which contains Ni^{2+} cations surrounded by an octahedral array of acrylonitrile ligands, accompanied by $Zn_2Cl_6^{2-}$ anions [15]. The ligand geometry, together with bond distances and angles, is shown in Fig. 4, which also lists related data for the methacrylonitrile complex $CuBr(NCCMeCH_2)$ [16]. Unfortunately the relatively large e.s.d.'s in the data for the nickel complex prevent detailed interpretation of the data, and no significance can be attached to the apparent differences between the two complexes.

The nickel complex incidentally was first prepared by use of a recipe (anhydrous $NiCl_2$ + excess acrylonitrile in the presence of Zn) that had been reported [19] to give a product of composition $NiCl_2 \cdot 2(NCCHCH_2)$. The incorporation of zinc in the product went undetected because the method of analysis used (EDTA titration) gave the total metal content rather than the

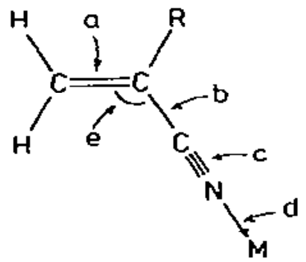


Fig. 4. Ligand geometry in the N-bonded complexes (i) $[Ni(N:CH:CH_2)_6]^{2+}$ $[Zn_2Cl_6]^{2-}$ and (ii) $CuBr(N:CMe:CH_2)$

	a (pm)	b (pm)	c (pm)	d (pm)	e (°)
(i)	125(7)	148(7)	113(5)	205(5)	120(2)
(ii)	133(2)	144(2)	113(2)	197(1)	120(1)

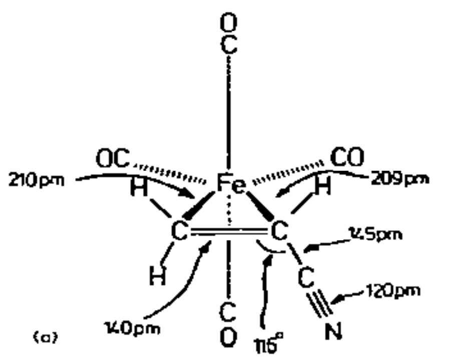
nickel content, which can be measured readily enough by the dimethylglyoxime method. An alternative synthesis of this mixed metal complex uses appropriate proportions of the anhydrous metal chlorides ($NiCl_2 + 2\ ZnCl_2$). Since the reaction of nickel(II) chloride and acetonitrile in the presence of zinc affords $[Ni(NCMe)_6]^{2+}[ZnCl_4]^{2-}$ [20], not $NiCl_2 \cdot 3$ MeCN as originally reported [19], zinc should be regarded as a likely constituent, as $ZnCl_4^{2-}$ or $Zn_2Cl_6^{2-}$, of the products of other nitrile adducts prepared by the zinc method (MCl_n + Zn + excess RCN) for which compositions $MCl_n \cdot x$-RCN have been reported [19].

The hexachlorodizincate anion $Zn_2Cl_6^{2-}$ in the complex $[Ni(NCCHCH_2)_6]^{2+}$ $[Zn_2Cl_6]^{2-}$ is itself interesting in that it is isostructural with the isoelectronic Al_2Cl_6 molecule, with tetrahedrally coordinated metal atoms bridged by pairs of chlorine atoms. Two other systems incorporating this anion accompanied by complex metal cations (not nitrile systems) have been characterized [21,22].

(iii) Type (b) complexes, bonded dihapto through the vinyl group

(a) The iron(0) complex (η^2-CH_2CHCN)$Fe(CO)_4$

The reaction of iron pentacarbonyl with acrylonitrile is interesting in that it affords products believed to illustrate all three known types ((a), (b) and (c)) of acrylonitrile coordination, viz. (η^1-CH_2CHCN)$Fe(CO)_4$ (type (a)), (η^2-CH_2CHCN)$Fe(CO)_4$ (type (b)), and (μ-CH_2CHCN)$Fe_2(CO)_6$ (type (c)) [23]. The structure of the second of these has been established by an X-ray crystallographic study [24] and is illustrated in Fig. 5. The coordination about the metal may be regarded as trigonal bipyramidal, with the acrylonitrile ligand occupying one of the equatorial sites. However, as the alkene function lies in the equatorial plane, an alternative description is



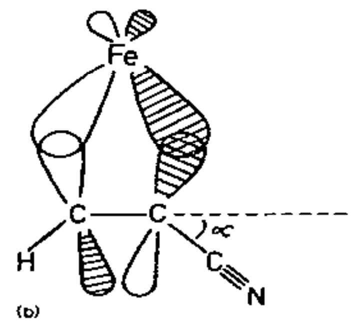


Fig. 5. Structure of (η^2-CH_2CHCN)$Fe(CO)_4$. (a) Distorted octahedral coordination about Fe, and bond distances. (b) Possible non-planar ligand geometry and implied orbital orientations.

possible in terms of distorted octahedral coordination about iron (Fig. 5a). Interestingly, the cyano group is folded back slightly (ca. 13°) away from the $Fe(CO)_4$ residue, a distortion that has been attributed to repulsion by the carbonyl ligands. An alternative and more likely explanation is that the orientation of the nitrile group is part of a general distortion from planarity of the alkene section of the ligand (the hydrogen atoms of which were not located) that would allow more effective overlap of the ligand and metal orbitals for back π-bonding (Fig. 5b). Such a distortion from planarity appears to be a general characteristic of alkene ligands, as the data in Table 1 illustrate.

(b) The nickel(0) complex (η^2-CH_2CHCN)$Ni[P(OR)_3]_2$ (R = ortho-tolyl) [33]

In this 16 electron zero-valent nickel complex and its ethylene analogue, (η^2-C_2H_4)$Ni[P(OR)_3]_2$, the two carbon and two phosphorus atoms coordinated to each nickel atom are very nearly coplanar, so the metal coordination may be regarded as trigonal, with the alkene ligand occupying one site, orientated with its C=C bond virtually in the NiP_2 plane, or alternatively as distorted square planar, with the alkene ligand occupying two adjacent sites (Fig. 6) [33]. The acrylonitrile and ethylene complexes differ slightly in the orientation of their phosphite ligands and in the slight departure of their skeletons from planarity. More significantly, they differ in their Ni–C bond lengths (Fig. 6). The acrylonitrile complex has Ni–C bonds some 5 pm

TABLE 1

Dihedral angle α (distortion from planarity) of alkene ligands coordinated to transition metals

Compound	Ligand	Dihedral angle α [a]	Ref.
$KPtCl_3(C_2H_4)\cdot H_2O$	C_2H_4	17°	25
$Nb(C_5H_5)Et(C_2H_4)$	C_2H_4	26°	26
$Rh(C_5H_5)(C_2F_4)(C_2H_4)$	C_2H_4	21°	27
$Rh(C_5H_5)(C_2F_4)(C_2H_4)$	C_2F_4	37°	27
$Ni(CNBu)_2[C_2(CN)_4]$	$C_2(CN)_4$	28°	28
$Pt(PPh_3)_2[C_2(CN)_4]$	$C_2(CN)_4$	32°	29
$Ir(PPh_3)_2(C_6N_4H)(CO)[C_2(CN)_4]$	$C_2(CN)_4$	34°	30
$Ir(PPh_3)_2Br(CO)[C_2(CN)_4]$	$C_2(CN)_4$	35°	31
$Pt(PPh_3)_2[Cl_2CC(CN)_2]$	$Cl_2CC(CN)_2$	20°, 42°	32
$Fe(CO)_4(CH_2CHCN)$	CH_2CHCN	13°	24
$Ni[P(OR)_3]_2(CH_2CHCN)$	CH_2CHCN	14°	33

[a] See Fig. 5b.

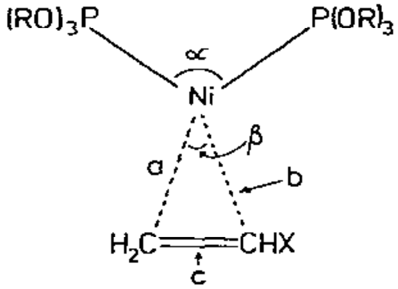


Fig. 6. Structures of (η^2-CH_2CHCN) $Ni[P(O\text{-tolyl})_3]_2$ and (η^2-C_2H_4) $Ni[P(O\text{-tolyl})_3]_2$

X	a (pm)	b (pm)	c (pm)	α (°)	β (°)
CN	202	191	146	110	43
H	202	202	146	116	43

shorter than those in the ethylene complex, and the acrylonitrile molecule is shifted along the C=C axis to bring the nitrile end of the molecule nearer to the nickel atom. Both of these differences can be attributed to electronic effects—the cyano group stabilizes the alkene π^* orbital and so strengthens the Ni(d) →C= C(π^*) back π-bonding.

The orientation of the cyano group in (η^2-CH_2CHCN)$Ni[P(OR)_3]_2$, like that in (η^2-CH_2CHCN)$Fe(CO)_4$, is consistent with a slight folding (ca. 14°) away from the metal of the substituents on the alkene carbon atoms, a distortion again attributable either to non-bonded repulsions or to better orbital overlap for back π-bonding (see Fig. 5b and Table 1).

(iv) Type (c) complexes containing bridging acrylonitrile ligands: the molybdenum(0) complex $Mo_2(CO)_4(PBu_3)_4(\mu\text{-}CH_2CHCN)_2$ and the copper(I) complex $Cu_2Cl_2(\mu\text{-}CH_2CHCN)$

The shape of the acrylonitrile molecule precludes simultaneous coordination to the same acceptor atom through both the nitrogen 'lone pair' and the vinyl group. However, bridging between two metal atoms, of the type shown in Fig. 2c, appears to be quite a common state of coordination for acrylonitrile, and has been confirmed by X-ray studies on the molybdenum(0) complex $Mo_2(CO)_4(PBu_3)_4(\mu\text{-}CH_2CHCN)_2$ (Fig. 7) [34] and on the copper(I) complex $Cu_2Cl_2(\mu\text{-}CH_2CHCN)$ (Fig. 8) [35].

The centrosymmetric molecules of the former consist of pairs of $Mo(CO)_2(PBu_3)_2$ units bridged by pairs of acrylonitrile ligands (Fig. 7) [34]. The coordination about each metal atom is effectively octahedral if the

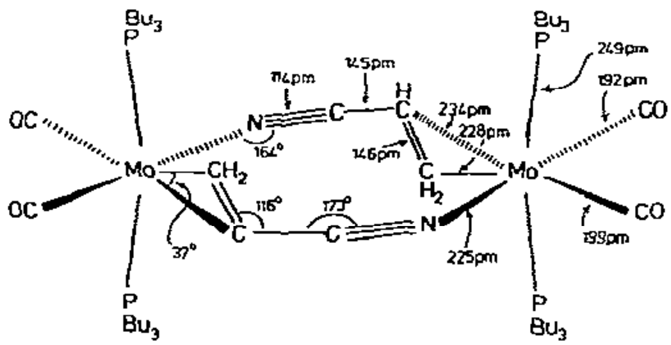


Fig. 7. Structure of $Mo_2(CO)_4(PBu_3)_4(\mu\text{-}CH_2CHCN)_2$.

alkene function is taken to occupy one coordination site. The orientations of the acrylonitrile functional groups with respect to the bridged metal atoms show slight departures from ideality (note the Mo–C bond lengths, and the non-linear MoNC and NCC units) that are presumably a consequence of the need to accommodate two bridging molecules to confer an 18 electron configuration on the metal atoms.

The bridging acrylonitrile ligands in $Cu_2Cl_2(\mu\text{-}CH_2CHCN)$ (Fig. 8) [35] by contrast can adopt an unstrained orientation with respect to the bridged metal atoms, which though both copper(I), are of two distinct types. Those coordinated to the alkene functions also have two chlorine atoms attached in a pseudotrigonal array. Those coordinated to the nitrile function also have three attached chlorine atoms in a tetrahedral array.

(v) Bond lengths in acrylonitrile adducts

The lengths of the bonds in specific adducts have been given in Figs. 4–8. Selected bond lengths are listed in Table 2 for purposes of comparison.

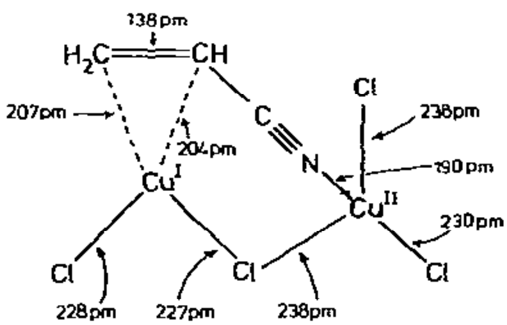


Fig. 8. Ligand geometry in $Cu_2Cl_2(\mu\text{-}CH_2CHCN)$.

TABLE 2

Bond lengths (pm) in acrylonitrile adducts

Compound [a]	$M-C^1$	$M-C^2$	M–N	$C^1{=}C^2$	C^2-C^3	$C^3\equiv N$	Ref.
Free L	–	–	–	133.9(1)	142.6(1)	116.3(1)	18
$NiL_6Zn_2Cl_6$	–	–	209(3)	121(6)	157(5)	107(4)	15
L′CuBr	–	–	197(1)	133(2)	144(2)	113(2)	16
$LFe(CO)_4$	210(1)	209(2)	–	140(2)	145(2)	120(2)	24
$LNi[P(OR)_3]_2$	202(1)	191(1)	–	146(2)		114(2)	33
$L_2Mo_2(CO)_4(PBu_3)_4$	228(1)	234(1)	225(1)	146(1)	145(1)	114(1)	34
LCu_2Cl_2	207(1)	204(1)	190(1)	138(2)		115(1)	35

[a] $L = C^1H_2{=}C^2H{-}C^3\equiv N$; $L' = C^1H_2{=}C^2Me{-}C^3\equiv N$; R = *ortho*-tolyl; e.s.d's in parentheses.

Although the e.s.d.'s are too high to allow detailed discussion of the data, one feature is clearly apparent. Coordination through the vinyl group invariably lengthens the C=C bond of acrylonitrile, as electronic charge is effectively transferred from the ligand HOMO (π-bonding) to the ligand LUMO (π-antibonding). Whether the nitrile C≡N bond also changes in length on coordination cannot be inferred from the data in Table 1. It too might be expected to lengthen slightly on account of back π-bonding, though coordination through the nitrogen 'lone pair', actually feebly C–N antibonding, would have the opposite effect [36,37].

A more sensitive guide to the type of changes that occur in the C=C and C≡N bonds of acrylonitrile on coordination is provided by the vibrational spectra, as discussed below.

C. FEATURES OF THE SPECTRA OF ACRYLONITRILE ADDUCTS

(i) Type (a) complexes, bonded through the nitrile nitrogen

When a nitrile RC≡N coordinates to a Lewis acid MX_n through the nitrogen 'lone pair', this can generally be detected by the characteristic increase that occurs in the nitrile stretching frequency, ν(C≡N), in the infrared spectrum [2,3,9] which arises from two effects. One is the coupling

TABLE 3

Characteristic absorptions (cm^{-1}) in the infrared spectra of some N-bonded acrylonitrile adducts L_mMX_n [a]

Compound	ν(C≡N)	$\Delta\nu$(C≡N)	$\tau(CH_2)$	$\omega(CH_2)$	ν(C=C)	Ref.
L	2230	0	975	975	1608	40
$LAlCl_3$	2291	+61	958	993	–	40
$LAlEt_3$	2276	+46	963	989	–	40
$LMnCl_2$	2252	+22	962	975	1603	41
$LFeCl_2$	2257	+27	961	975	1600	41
L_2ZnCl_2	2280	+50	962	994	1602	40, 41
L_2TiCl_4	2275	+45	964	990	1603	40
L_2SnCl_4	2255	+25	947	978	1595	40, 41
L_3CrCl_3	2268	+38	972	999	1600	41
$LCr(CO)_5$	2252	+32	–	–	–	42
$LW(CO)_5$	2244	+14	–	–	–	42
$L[C_6H_4(OAc)_2]Cr(CO)_2$	2227	−3	–	–	–	42
$L(C_6H_6)Cr(CO)_2$	2197	−33	–	–	–	42

[a] L = CH_2CHCN; $\Delta\nu$(C≡N) is the nitrile stretching frequency increase on coordination.

of this vibration with that of the new dative N → M bond, with which the C≡N bond is colinear, and which will be compressed as the C≡N bond is stretched. The other is the slight strengthening of the C≡N bond already alluded to, as the weakly antibonding character of the nitrogen 'lone pair' orbital decreases when it becomes the N → M bonding orbital [36–39].

Table 3 lists spectroscopic data for a series of acrylonitrile adducts [40–42] all of which are believed to have structures of type (a). The shift to higher frequency of the nitrile stretching absorption varies markedly with the Lewis acid MX_n involved, and indeed two of the adducts listed have nitrile stretching frequencies lower than that (2230 cm^{-1}) of uncoordinated acrylonitrile. Significantly, these involve soft Lewis acids capable of back π-bonding to the nitrile to a sufficient extent to offset the frequency-increasing factors described [42].

Also listed in Table 3 are the frequencies of bands attributable to other vibrations of coordinated acrylonitrile, including the alkene stretching vibration, $\nu(C{=}C)$, and the twisting $\tau(CH_2)$ and wagging $\omega(CH_2)$ vibrations of the methylene group. These last absorptions provide a further guide to the state of coordination of acrylonitrile. The methylene twisting and wagging absorptions of free acrylonitrile are exactly superimposed at 975 cm^{-1}. On coordination, however, these absorptions separate, $\tau(CH_2)$ decreasing and $\omega(CH_2)$ increasing in frequency, effectively as the canonical form $^{\oplus}CH_2{-}CH{=}C{=}N{-}MX_n^{\ominus}$ acquires significance [41,43]. For example, the adduct $SnCl_4 \cdot 2NCCHCH_2$ has $\tau(CH_2) = 947$ cm^{-1} and $\omega(CH_2) = 978$ cm^{-1}. Since electron withdrawal from the methylene carbon atom, i.e. the significance of the above canonical form, will increase with the electron withdrawing properties of the Lewis acid MX_n, the separation of $\tau(CH_2)$ and $\omega(CH_2)$ can be used as a guide to the relative Lewis acidities of different acids MX_4 [40].

The vibrational spectra of adducts $MX_n \cdot x$-$NCCHCH_2$ have also been used to investigate the stereochemistry at M. The spectra of adducts $MX_5 \cdot NCCHCH_2$ (M = Ta, Nb [43,44] or Sb [45]), $MX_4 \cdot 2NCCHCH_2$ (M = Ti, Zr, Nb, Ta [43,44] or Sn [46]) and $MX_3 \cdot 3NCCHCH_2$ (M = Ti, V [43,44] Cr [41] or Mo [47]) are consistent with octahedral coordination about the metal, and detailed analyses of the far infrared, Raman and nuclear quadrupole resonance spectra have shown the tetrahalide adducts to have a *cis* stereochemistry [43,44,48], while for the trihalide adducts a *meridial* configuration is indicated [43,44].

Further information on N-bonded acrylonitrile complexes has been obtained from nuclear magnetic resonance spectroscopic studies, though these have been far fewer in number than the vibrational spectroscopic studies. Work to date has identified the likely electronic origins of the changes in chemical shifts that occur when acrylonitrile coordinates through nitrogen [49].

The three olefinic protons of uncoordinated acrylonitrile give rise to an ABC-type pattern of peaks under normal resolution centred at ca. $\delta = 6.0$ p.p.m. downfield from T.M.S. [50]. Coordination through nitrogen is usually accompanied by a small downfield shift of ca. 0.1–0.5 p.p.m. in the resonance attributable to the α-hydrogen atom. A similar shift in the α-hydrogen resonance on coordination is shown by saturated nitriles and is attributed to the electron-withdrawing inductive effect of the Lewis acid. The effect of coordination on the position of the β-hydrogen resonances is less clearcut; these may shift either way [49] or not at all [51]. They appear to be subject to two opposing influences. The inductive effect discussed above in connection with the α-hydrogen resonance is unlikely to be responsible for the whole of the downfield shift, 0.428 p.p.m. in the case of the *cis* proton in the cationic complex $[(NH_3)_5Rh(N{\equiv}CCH{=}CH_2)]^{3+}$ [49], in which the dominant deshielding effect probably arises from polarization of the π-bond, the canonical form $^{\oplus}CH_2{-}CH{=}C{=}N{-}^{\ominus}MX_n$ becoming significant. An opposing effect which could lead to a net shielding of the β-protons would be release of electronic charge from a *d* orbital of the acceptor MX_n into the empty π^* ligand MO. Consideration of the coefficients of this MO (Fig. 3) shows that most of the charge released into this orbital will be associated with the olefin function and so provide the necessary shielding.

Even when the structure of an adduct in the crystal has been established different structures may obtain in solution, where complex equilibria may operate. The behaviour of a metal halide in nitrile solution (from which adducts are commonly crystallized) is governed by a number of factors, including the dielectric constant and basicity of the solvent, the Lewis acidity and maximum coordination number of the acceptor atom of the solute and the susceptibility of its M–X bonds to solvolytic cleavage. Few rigorous studies have been carried out to probe the detailed behaviour of metal halides in acrylonitrile, though aluminium trichloride is known to undergo solvolysis in acrylonitrile—^{1}H and ^{27}Al NMR spectroscopic studies [52] have indicated the presence of such ions as $Al(NCCHCH_2)_6^{3+}$ and $AlCl_4^-$. The possible complexity of such systems has been revealed by a careful study of the $AlCl_3$–acetonitrile system [53] by ^{1}H, ^{27}Al NMR, infrared and Raman spectroscopy and X-ray crystallography which indicated that many solution species were involved and that the adduct $AlCl_3 \cdot 3NCMe$, isolated from solution, instead of having a covalent *mer* octahedral structure as might have been expected, actually has the structure $[AlCl(NCMe)_5]^{2+}[AlCl_4^-]_2 \cdot MeCN$.

Our own investigations [15] and those of others [19,20] have shown that nickel(II) chloride in the presence of zinc or zinc chloride undergoes solvolysis in nitriles to form ionic products such as $[Ni(NCMe)_6]^{2+}[ZnCl_4]^{2-}$ or $[Ni(NCCHCH_2)_6]^{2+}[Zn_2Cl_6]^{2-}$, and solvolytic dissociation of the Lewis acid also appears to occur in zinc chloride– and cobalt chloride–acrylonitrile systems [54–56]. However, solvolytic cleavage of the Lewis acid to form ionic products has not been detected by conductivity studies on acrylonitrile solutions of $TiCl_4$, $SnCl_4$ or $SbCl_5$ [43–46], which may be less susceptible to such reactions because of their greater M–Cl bond strengths: E(M–Cl) = 494 kJ mol^{-1} for Ti, 414 kJ mol^{-1} for Sn; cf. 230 kJ mol^{-1} for Zn [57,58].

(ii) Type (b) and (c) complexes, bonded through the alkene function or bridging

The effect of coordination through the alkene function on the vibrational spectrum of acrylonitrile is illustrated by the data in Table 4 [34,42,57,59–63]. The most significant effect is that the alkene stretching frequency ν(C=C), 1608 cm^{-1} for free acrylonitrile, invariably drops by at least 90 cm^{-1} as the C=C bond order falls. However, assignment difficulties often arise as the absorption moves into a region obscured by other vibrations such as C–H bending modes or even C–C single bond stretching absorptions.

Much interest has focused on the zero-valent nickel complex $Ni(CH_2CHCN)_2$ because of the bonding problems it poses, and because of its catalytic activity in cycloaddition and related reactions, as discussed in Section E below. It is readily prepared by refluxing acrylonitrile with nickel tetracarbonyl [64]. Addition of triphenylphosphine affords the mixed complexes [65,66] $Ni(PPh_3)(CH_2CHCN)_2$ and $Ni(PPh_3)_2(CH_2CHCN)_2$. In this

TABLE 4

Characteristic absorptions (cm^{-1}) in the infrared spectra of some π-bonded acrylonitrile adducts

Compound [a]	ν(C≡N)	$\Delta\nu$(C⋮N) [b]	ν(C=C)	Ref.
L	2230	–	1608	
$LNi[P(OR)_3]_2$	2194	−36	?	59
$LFe(CO)_4$	2226	−4	?	60
LCu_2Cl_2	2217	−13	1502	61
$(\mu L)_2Mo_2(CO)_4(PBu_3)_4$	2219, 2212	−11, −18	<1465	34
L_2Ni	2220	−10	1446	62
$L_2Ni(PPh_3)$	2191	−39	?	62
$L_2Ni(PPh_3)_2$	2175	−55	?	62
$LPt(PPh_3)_2$	2195	−35	?	63
$L_3W(CO)_3$	2221	−9	1440	51
$L_3Mo(CO)_3$	2225	−5	1456	51
$L(C_6Me_3H_3)Cr(CO)_2$	2197	−33	?	42
$L(C_6Me_6)Cr(CO)_2$	2195	−35	?	42

[a] L = CH_2CHCN; R = *ortho*-tolyl.
[b] $\Delta\nu = \nu(C{\equiv}N)_{adduct} - \nu(C{\equiv}N)_L$.

last compound there appears little doubt that the nitrile ligands coordinate dihapto through their vinyl groups, a mode of coordination also likely in $Ni(CH_2CHCN)_2$ and $Ni(PPh_3)(CH_2CHCN)$, though probably also supplemented by coordination through the nitrile nitrogen atom in these last two cases. A crystallographic study of one or more of these complexes would be helpful.

In addition to the decrease in $\nu(C{=}C)$ already referred to, coordination through the vinyl group of acrylonitrile also causes the methylene twisting and wagging absorptions, $\tau(CH_2)$ and $\omega(CH_2)$, to shift to lower frequencies, in contrast to the effect caused by coordination through the nitrile group alluded to above. The nitrile stretching frequency also may decrease slightly because of back π-bonding from the metal into the vinyl π^* orbital (the LUMO), which, as already mentioned, has slight $C{\equiv}N$ π^* character. This feature is clearly illustrated by the nickel adducts $Ni(CH_2CHCN)_2$, $Ni(PPh_3)(CH_2CHCN)$ and $Ni(PPh_3)_2(CH_2CHCN)_2$ (Table 4). When acrylonitrile alone coordinates to nickel, scope for back π-bonding is less than when one or two phosphine ligands are present. An alternative explanation for the stepwise decrease in $\nu(C{\equiv}N)$ for this series of nickel complexes is that in $Ni(CH_2CHCN)_2$ and possibly in $Ni(PPh_3)(CH_2CHCN)_2$, the nitrile group is also coordinated through its nitrogen atom, giving the ligand a bridging (type (c)) geometry like that in $Cu_2Cl_2CH_2CHCN$ [35] and $Mo_2(CO)_4(PBu_3)_4(CH_2CHCN)_2$ [34].

The ^1H and ^{13}C NMR spectra of acrylonitrile complexes coordinating through the vinyl group show upfield shifts of the olefinic nuclei relative to the free nitrile. The magnitude of the shift varies markedly with the Lewis acid, but is sufficient to distinguish this mode of bonding from type (a) complexes, which, as already described, show a downfield shift of the α-proton resonance. Similar upfield shifts are shown by most alkenes when coordinated to transition metals and are interpretable on the Dewar [67]–Chatt–Duncanson [68] back π-bonding model, though the magnitude of the shift alone should not be taken as a guide to the extent of $d \rightarrow \pi^*$ back bonding [69]. However, the general correlation between the decrease in $\nu(C{=}C)$ in the infrared spectrum and the decrease in $\delta(^1H)$ and $\delta(^{13}C)$ in the NMR spectrum on coordination for a wide variety of alkenes [4] suggest that both types of spectra provide useful indications of the metal–alkene interactions.

D. THE LEWIS BASICITY OF ACRYLONITRILE

(i) Basicity of the nitrile function

The Lewis basicity of nitriles RCN is relatively insensitive to the bulk of the group R, because the site of coordination, the nitrile nitrogen atom, is relatively remote from the group R. The most important factor that influences the stability to dissociation of nitrile adducts is the electronegativity of the substituent R. Electron-withdrawing groups on the nitrile reduce the stability of adducts, while electron-releasing groups strengthen the coordinate link. By comparison with other organic groups R, the vinyl group is relatively neutral in this respect. The ^{121}Sb Mössbauer [70] and vibrational spectra [45] of a series of antimony pentachloride adducts $SbCl_5$, NCR are consistent with increasing Lewis basicity in the series:

$$R = CCl_3 < CH_2Cl < CH:CH_2 \sim Et \sim Bu^t < Ph \sim (CH_2)_3CN \sim (CH_2)_4CN$$

A ^{35}Cl NQR study [48] on related adducts has led to the following Lewis base sequence:

$$1{,}2\text{-}C_6H_4(CN)_2 < NCCH_2CN < MeCN < PhCN \sim CH_2CHCN \sim Bu^tCN$$

Another series of relative basicities has been obtained from studies [71] of the displacement equilibria set up when pairs of nitriles compete for coordination to niobium(V) or tantalum(V) chloride:

$$RCN, MCl_5 + R'CN \rightleftharpoons R'CN, MCl_5 + RCN$$

These studies led to the following Lewis base sequence:

$$FCH_2CN < ClCH_2CN < BrCH_2CN < ICH_2CN \ll ClC_6H_4CN \sim CH_2CHCN$$
$$< PhCN < MeCN \sim Bu^tCN$$

Yet another approach to the measurement of relative basicities has been to explore the deviation from ideality of the vapour pressures of binary mixtures of $SiCl_4$ or $GeCl_4$ and the Lewis bases in question [72,73]. The sequence $MeCN < CH_2CHCN < EtOAc < THF$ was indicated by these measurements, which provided several totally unexpected and apparently unprecedented examples (including the $CH_2CHCN/SiCl_4$ and $CH_2CHCN/GeCl_4$ systems) of acid-base mixtures that show positive deviations from ideality. Acrylonitrile absorbs rather than evolves heat when mixed with $SiCl_4$ or $GeCl_4$, and the mixtures have remarkably high vapour pressures. Evidently acrylonitrile molecules associate preferentially with their own kind rather than with these tetrahalide molecules, which would need to distort appreciably to allow bonding to the nitrile nitrogen atoms, a distortion that can occur only if the energy of the dative bond formed exceeds the reorganization energy involved. Acrylonitrile and similar weak base molecules coordinate too feebly to cause $SiCl_4$ or $GeCl_4$ molecules to distort to accommodate them, even though with $SnCl_4$ molecules they form isolable adducts $SnCl_4 \cdot 2\,CH_2CHCN$, etc.

(ii) Basicity of the alkene function

In considerations of the capacity of acrylonitrile to coordinate through its alkene function, it is important to bear in mind that the stability of alkene complexes depends not only on the capacity of the ligand to release electronic charge to the metal atom from its π-bonding MO, but also on its capacity to withdraw electronic charge from the metal atom into its π^* antibonding MO. This latter factor, the π-acid property, is particularly important in alkenes, like acrylonitrile, that have electron-withdrawing substituents.

Various methods have been used to determine the coordinating power of acrylonitrile as an alkene ligand. For example, studies of ligand displacement equilibria of the type:

$$\mathrm{Ni[P(OR)_3]_3 + alkene \rightleftharpoons [alkene]Ni[P(OR)_3]_2 + P(OR)_3}$$

have shown the coordinating power of alkenes towards the Lewis acid $\mathrm{Ni[P(OR)_3]_2}$ (R = *ortho*-tolyl) to increase in the following sequence [59,74,75]:

$$\mathrm{C_2H_4 < CH_2{=}CHCO_2Me < CH_2{=}CHCN \sim MeO_2CCH{=}CHCO_2Me}$$
$$\mathrm{< NCCH{=}CHCN < O\overline{CCH{=}CHCO\cdot O}}$$

In another study [76], using iridium complexes of the general formula $\mathrm{Ir(CO)(PPh_3)_2X,L}$ (X = Cl, Br, I, NCS or NO; L = alkene), carbonyl stretching frequencies as well as ligand replacement reactions were used to show that the Lewis basicity of some cyano-alkenes increased in the sequence

$$\mathrm{PhCH{=}CHCN < CH_2{=}CHCN < NCCH{=}CHCN < (NC)_2C{=}C(CN)_2}$$

Both sequences are consistent with an increase in coordinating power as

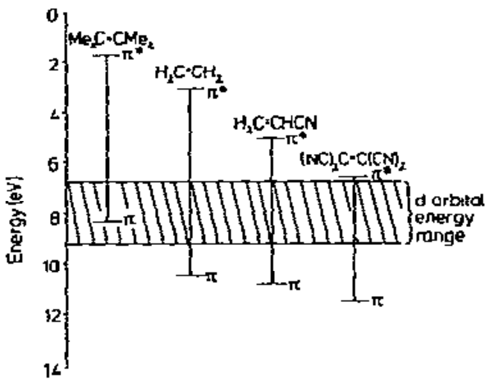


Fig. 9. π and π^* orbital energy levels of some selected olefins contrasted with a typical range of transition metal valence *d* orbital first ionization potentials.

the hydrogen atoms of C_2H_4 are replaced by electron-withdrawing substituents such as the nitrile group CN or carboxylic ester residue CO_2Me. Such substituents lower the energies of both the π-bonding and π^*-antibonding orbitals of the alkene, thereby reducing its donor properties to some extent, but increasing its acceptor properties to a greater extent, since the energy of the π^*-orbital falls more than that of the π-orbital (Fig. 9). Acrylonitrile forms more stable adducts than does ethylene because it is a significantly stronger π-acid ligand than the latter, though a less powerful electron-donor.

E. REACTIONS INVOLVING COORDINATED ACRYLONITRILE

When coordinated to a Lewis acid, acrylonitrile may show enhanced reactivity to certain types of reagent, for example undergoing nucleophilic attack at the nitrile carbon atom more readily when coordinated through the nitrile nitrogen atom in a type (a) complex. Such reactions may broadly be classified according to the change they induce in the nitrile. This may suffer reduction of one or both of its unsaturated linkages, e.g. by insertion of that linkage into a metal–hydrogen or metal–carbon bond, or couple with one or more other acrylonitrile units in an oligomerization or polymerization reaction. Such reduction or coupling reactions are not mutually exclusive—oligomerization or polymerization usually involves simultaneous reduction of at least one of the unsaturated linkages—but are treated separately below for convenience.

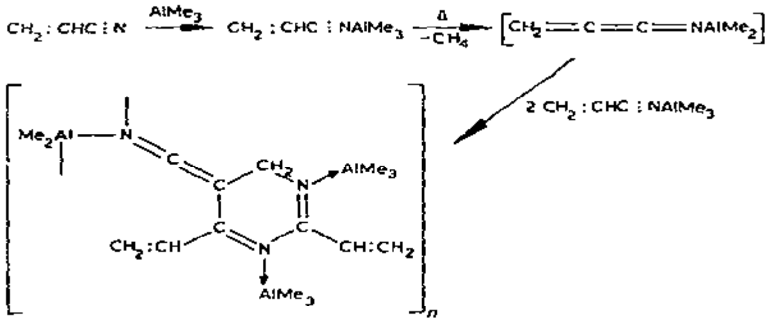
(i) Reduction reactions of coordinated acrylonitrile

Acrylonitrile reacts with dialkylaluminium hydrides to form vinylaldiminoaluminium dialkyls, probably via unstable adducts $CH_2{:}CHC{:}N, AlHR_2$ which, however, have not been isolated [77]. The free imine $CH_2{:}CHCH{:}NH$ is reportedly isolable from such reactions by treatment of the iminoalane with a weak acid such as acetylacetone:

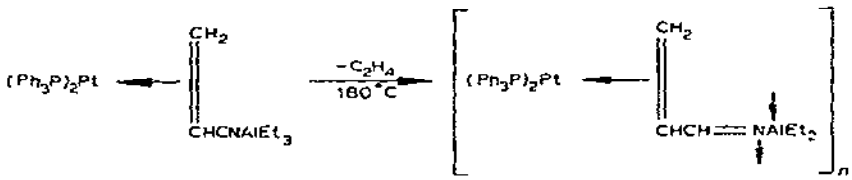
$$CH_2{:}CHC{:}N \xrightarrow{HAlBu^i_2} \left[CH_2{:}CHC{:}NAlHBu^i_2\right] \rightarrow \tfrac{1}{2}(CH_2{:}CHCH{:}NAlBu^i_2)_2$$

$$\xrightarrow[Hacac]{-5°C} CH_2{:}CHCH{:}NH + Al(acac)_3 + 2C_4H_{10}$$

Insertion of the nitrile function into a metal–carbon bond occurs less readily than into a metal–hydrogen bond, so when acrylonitrile is treated with an aluminium trialkyl, e.g. $AlMe_3$, the N-bonded adduct $CH_2{:}CHC{:}NAlR_3$ can be isolated [78,79]. When heated, this adduct does not simply rearrange like its hydride analogue, but loses methane in a reaction in which oligomerization of the nitrile is believed to occur, leading to complex products containing various structural units. The following equation presents an idealized version of the type of product believed to result.



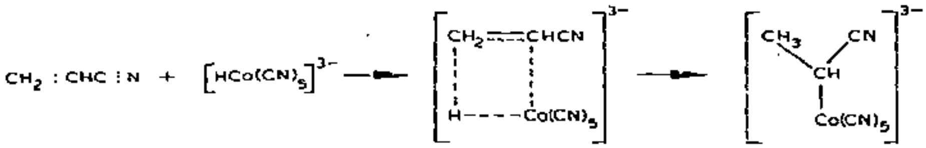
A much cleaner reaction occurs if acrylonitrile coordinates simultaneously through its nitrogen atom to triethylaluminium and through its vinyl group to platinum. The mixed metal complex $(Ph_3P)_2PtCH_2CHCNAlEt_3$ is itself isolable and readily characterized. When heated to ca. 180°C, it evolves ethylene, not ethane, forming a polymeric product in which the nitrile function has suffered hydroalumination.



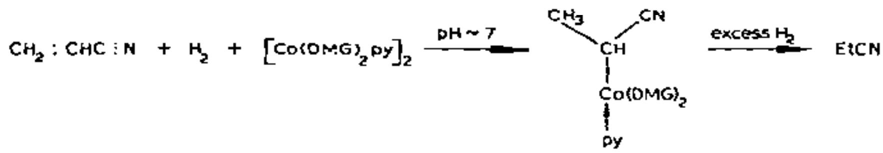
By contrast, alkyltin hydrides add to the C=C double bond of acrylonitrile, rather than to the nitrile function [80–83]. The metal may become attached either to the α or β carbon atom [82]

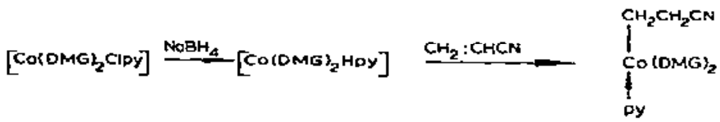
$$CH_2{:}CHC{:}N + R_3SnH \rightarrow \underset{\alpha}{R_3SnCH(Me)CN} + \underset{\beta}{R_3SnCH_2CH_2CN}$$

Addition of a source of free radicals increases the rate of formation of the β-metallated product but has no effect on the rate of formation of the α-metallated product, whereas the rate of formation of the latter is enhanced by increased solvent polarity. This suggests that the β-metallated product results from addition of the radicals $H^{\cdot}$ and $R_3Sn^{\cdot}$, whilst the α-metallated product results from electrophilic attack by $R_3Sn(\delta+)$–$H(\delta-)$, involvement of an intermediate adduct being uncertain. The C=C double bond of acrylonitrile is also reduced by the hydridopentacyanocobalt(III) anion $[HCo(CN)_5]^{3-}$, which affords the α-metallated product $[NCCH(Me)Co(CN)_5]^{3-}$ in a reaction for which some form of four-centre

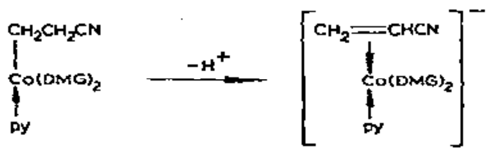


intermediate appears to be involved [12,13,84]. Cyanoethyl-cobalt species also result from the reduction of acrylonitrile by dimethylglyoximato-cobalt(III) base complexes such as the pyridine adducts $[Co(DMG)_2py]_2$ or $[Co(DMG)_2Clpy]$ (DMG = the dimethylglyoximato residue) [85]. In neutral solution, the α-metallated product predominates; in alkaline solution, the





β-metallated species is the major product. Under strongly alkaline conditions the β-metallated product suffers deprotonation and rearranges to the alkene π-complex form [86].



A variety of different reaction pathways has been found in studies of reactions between low-valent transition metal hydrides and acrylonitrile. Whilst cyclopentadienyliron dicarbonyl hydride, $(C_5H_5)Fe(CO)_2H$, reacts smoothly with acrylonitrile to give the α-metallated product $(C_5H_5)Fe(CO)_2CH(Me)CN$ without apparent intermediate adduct formation [87], the iridium hydride $HIr(PPh_3)_3CO$ affords a type (b) π-complex which rearrange to the β-metallated propionitrile only in the presence of an excess of acrylonitrile [88].

$$CH_2{:}CHC{:}N \xrightarrow[-PPh_3]{HIr(PPh_3)_3CO} HIr(PPh_3)_2(CO)(CH_2{:}CHCN) \xrightarrow[(CO)]{\text{excess } CH_2{:}CHCN} \underset{\underset{CH_2=CHCN}{\uparrow}}{(Ph_3P)_2Ir}{-}CH_2CH_2CN$$

Similarly, the dihydride $(C_5H_5)_2MoH_2$ will reduce only one molar proportion of acrylonitrile at low concentrations of acrylonitrile, though addition of an excess leads to elimination of propionitrile and formation of the π-complex [89]

$$(C_5H_5)_2MoH_2 \xrightarrow{CH_2:CHCN} (C_5H_5)_2MoH(CH_2CH_2CN) \underset{CH_2CHCN}{\xrightarrow{excess}}$$

$$(C_5H_5)_2Mo \leftarrow \begin{matrix} CH_2 \\ \| \\ CH \\ CN \end{matrix} + EtCN$$

Acrylonitrile may be activated towards carbanionic addition (to the β-carbon atom) by coordination to pentammine complexes of Co(III), Ru(III) and Rh(III). This allows catalytic addition of weak acids such as acetylacetone or nitromethane [90]:

$$[(NH_3)_5MNCCHCH_2]^{3+} \xrightarrow{[CH_2NO_2]^-} [(NH_3)_5MNCCHCH_2CH_2NO_2]^{2+} \xrightarrow{H^+} [(NH_3)_5M(NCCH_2CH_2CH_2NO_2)]^{3+}$$

The nitrile function of acrylonitrile inserts into the metal–chlorine bonds of tungsten hexachloride to afford a product containing a tungsten–nitrogen multiple bond [91]

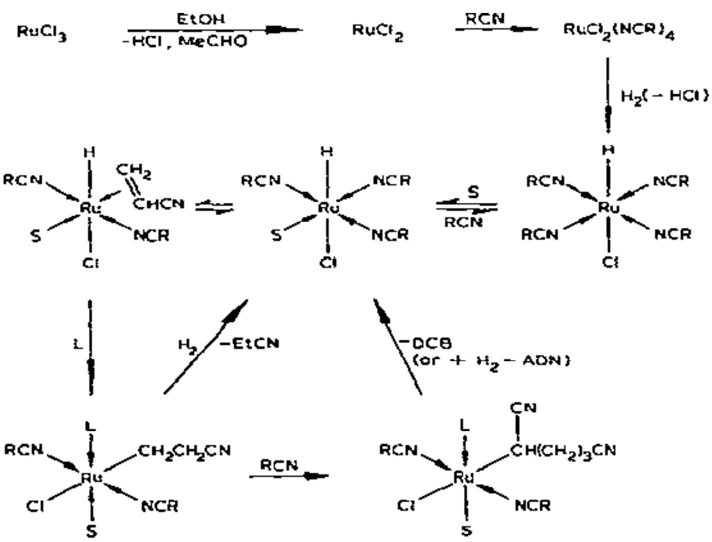
$$CH_2:CHC\vdots N + WCl_6 \rightarrow CH_2:CHCCl_2N \equiv WCl_4$$

(ii) Oligomerization reactions of acrylonitrile

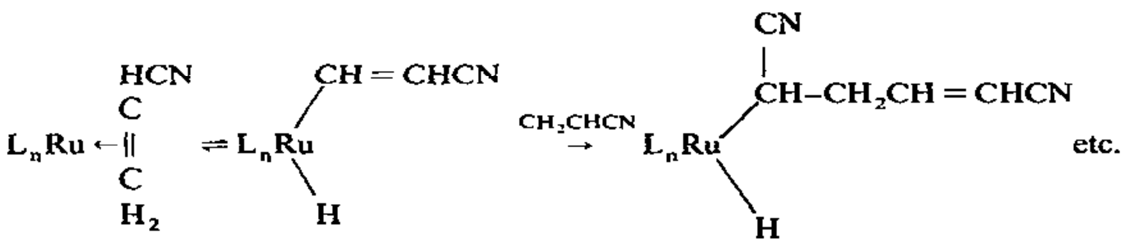
In this section, attention is focused primarily on dimerization reactions of acrylonitrile, the mechanisms of which tend to set the pattern for other oligomerization or polymerization reactions. Trimers and hexamers are common (unwanted) by-products of dimerization reactions.

Dimerization of acrylonitrile can afford the dicyanobutenes $NCCH=CHCH_2CH_2CN$ (DCB1), $NCCH_2CH=CHCH_2CN$ (DCB2), or $CH_2=C(CN)CH_2CH_2CN$ (methylene glutaronitrile, MGN). Reductive dimerization can afford adiponitrile, $NC(CH_2)_4CN$ (ADN), and oxidative dimerization can give dicyanobutadiene, $NCCH=CHCH=CHCN$ (DCBD). Here, we shall be concerned mainly with dimerization induced by metal salts or coordination complexes. Dimerization has also been effected by use of electrochemical techniques [92–94] and using phosphorus compounds as catalysts [92,95].

The most thoroughly studied metal systems have been those using ruthenium salts and complexes [96–107]. Compounds of Ru(II) or Ru(III) in the presence of hydrogen readily catalyse the reductive dimerization of acrylonitrile to adiponitrile, or dimerization to dicyanobutene, as shown principally by Misono and his co-workers [96–99] whose studies have indicated that N-bonded (type (a)) and π-bonded (type (b)) acrylonitrile complexes are involved in the catalytic cycle as well as β-cyanoethyl derivatives, as illustrated by the following reaction scheme. In this scheme, which is



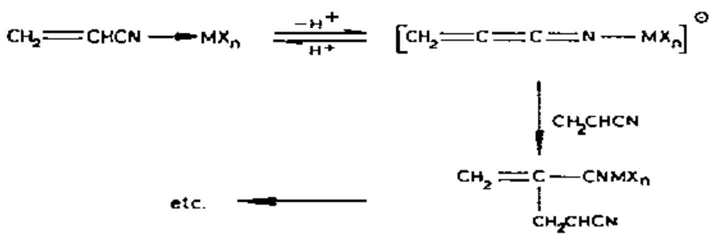
supported by deuteration studies, RCN = CH_2CHCN, S = solvent, and L is a 2-electron ligand that may be S, RCN or some other added ligand. Notable features of the scheme include the rearrangement of a type (a) complex to a type (b) complex, believed to occur under the *trans* influence of a solvent ligand; formation of a β-cyanoethyl derivative from a metal–hydride π-complex; and insertion of a second acrylonitrile molecule into the metal–carbon bond of the β-cyanoethyl derivative. A related scheme has been suggested [100] for the dimerization of acrylonitrile catalysed by $RuCl_2(PPh_3)_3$ in the presence of *N*-methylpyrrolidine. Rearrangement of π-complexes to β-cyano*vinyl* metal hydrides may also occur in such reaction systems:



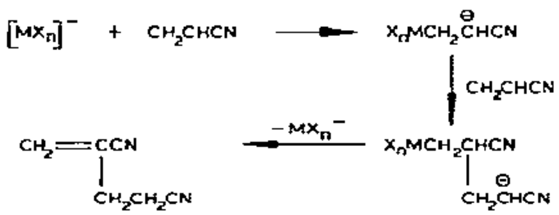
The disproportionation of acrylonitrile into propionitrile and dicyanobutadiene is another reaction catalyzed by ruthenium and platinum chloro complexes and presumably involving similar intermediate adducts, e.g. [108]

$$3\,CH_2CHCN \xrightarrow{RuCl_3 \cdot 3H_2O} EtCN + NCCH{=}CHCH{=}CHCN$$

Many metal halides catalyze the oligomerization of acrylonitrile to methylene glutaronitrile and 2,4,6-tricyanohexene in the presence of amines or isocyanides. Thus, the halides of Ti(IV), Cd(II), V(III), Al(III), Fe(II), Zn(II) and Co(II) catalyze the conversion of acrylonitrile into MGN in the presence of a tertiary amine [109,110]. The same systems codimerize acrylonitrile with acrylic esters in low yields, although acrylates alone were not dimerized. Various patents [111–114] suggest the range of catalysts based on these metals extends well beyond the halides. Copper oxide–alkyl isocyanide systems [115–116] are also effective catalysts for the formation of MGN. Quite how these various systems activate the α carbon atom of acrylonitrile to attack by the β-carbon atom of a second acrylonitrile molecule is not yet clear, though deprotonation of this α-carbon atom clearly must occur at some stage and is presumably facilitated by coordination (either through the nitrile nitrogen or the alkene function) to a suitable catalyst site, e.g.

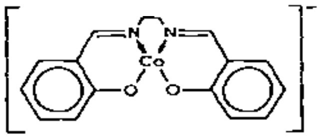


Alternatively,



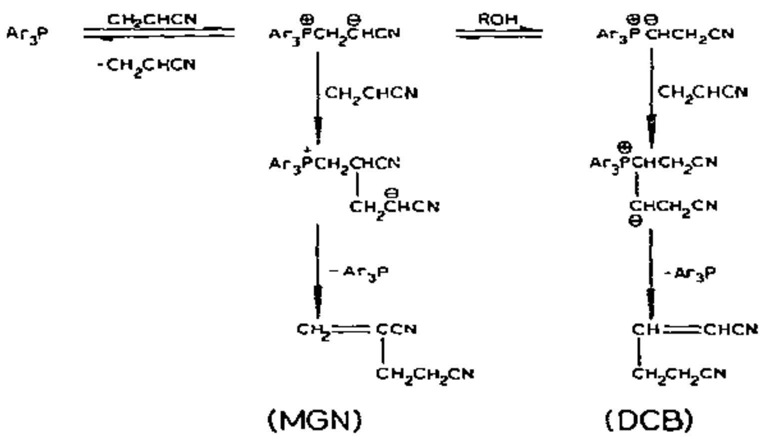
An example of an anionic metal complex that functions in this last manner is the cobalt N,N'-ethylenebis(salicylideneiminato)cobalt(I) complex [117].

In its mode of action, it resembles tertiary phosphine catalysts, which with acrylonitrile generate the betaine $R_3P^+CH_2^-CHCN$ [92,118]. Other nucleophiles that dimerize acrylonitrile 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 $LiAlH_4$ [119].



The phosphine catalysed acrylonitrile dimerizations noted earlier have featured frequently in the patent literature (see, e.g. refs. 120, 121) and are worthy of brief mention here. Like the systems just considered, the intermediates are strictly classifiable as acrylonitrile adducts only if the nitrile is regarded as the Lewis acid. Work during the 1960s using tri-alkyl and -aryl phosphines as catalysts showed that in the absence of protonic solvents such as alcohols, the main reaction is polymerization, occurring with explosive violence in the case of trialkylphosphines [92]. However, in alcohols, proton transfers occur readily enough to stop the reaction at the dimer stage. The dimeric product using trialkylphosphines is almost entirely MGN. With triarylphosphines, the reaction rate is much lower, and a higher proportion of DCB results.

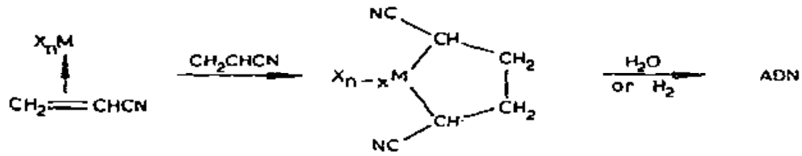
More recent studies using aryldialkylphosphonites $ArP(OAlk)_2$ and diarylalkylphosphinites Ar_2POAlk showed that high yields of linear dimers can be obtained under mild conditions [95]. Reaction is thought to proceed via the familiar betaine/ylid equilibrium, with MGN resulting from an attack by a second molecule of acrylonitrile on the betaine, whereas DCB results from attack by acrylonitrile on the ylid:



Non-catalytic dimerization of acrylonitrile has been effected by reacting a metal halide with a strongly reducing metal in a polar solvent [122–128], e.g.

$$CH_2CHCN + CoCl_2 + Mn \xrightarrow[\text{(ii) } H_2O]{\text{(i) } HCONMe_2} ADN$$

The yield is stoichiometric in the reducing metal consumed. The reaction may involve a metallacyclopentane intermediate:



(iii) Acrylonitrile complexes as catalysts

It was noted in the previous section that acrylonitrile complexes feature in several dimerization reactions of acrylonitrile catalysed by Lewis acids, and preformed complexes such as the ruthenium (II) chloride complex $RuCl_2(NCCH{=}CH_2)_4$ can themselves therefore be used as catalysts for such dimerization reactions [100]. The nickel complex $Ni(CH_2CHCN)_2$ catalyses a range of oligomerization and rearrangement reactions [7], and its activity as a catalyst for cycloaddition reactions has been exploited in several reactions of bicyclo(1,1,0)butanes with olefins [129–134]. The zinc chloride complex $ZnCl_2(NCCHCH_2)_2$ has also been used as a cycloaddition and polymerization catalyst [135–138].

F. TABULAR SURVEY

There has not been space in this review to discuss all the facets of acrylonitrile coordination chemistry that have been studied, but it is hoped that the chosen selection will have given some indication of the structures, properties and reactions of acrylonitrile adducts. To illustrate the range of Lewis acids towards which the coordination behaviour of acrylonitrile has been studied, we conclude this short review by a tabular survey listing the Lewis acids (arranged according to the position of the metal in the Periodic Table) and indicating what type of study these systems have been subjected to (Table 5).

TABLE 5

Systems investigated for Lewis acidity towards acrylonitrile

Lewis acid [a]	n [b]	Type of study		
		Spectra	Reactions	Misc.
Group IA				
LiCl	1			139
$LiNO_3$	1			139
LiMe	–			140
Group IIA				
$MgX_2 + R_3N$	–			112
(X=Cl, Br, I)				
$Mg(NO_3)_2$	1			139
$Mg(SbCl_6)_2$	6	141	141	
$Mg(InCl_4)$	3	141	141	
Group IIIA				
BCl_3	1	142, 143	144	
$BEtCl_2$	1	40		
$AlCl_3$	2	160		
	1	40, 150	40	
	–	40, 52, 150	109, 113	
$AlMeCl_2$	1	40, 78, 79	40, 78, 79	
$AlEtCl_2$	1	40, 146, 148	40	
		149, 150, 151		
$Al(OEt)Cl_2$	1	40	40	
$Al_2Et_3Cl_3$	–			136
$AlMe_2Cl$	1	78, 79	78, 79	
$AlEt_2Cl$	1	40	40, 305, 309	
$AlEt(OEt)Cl$	1	40	40	
$AlHBu^i_2$	–		77	
$AlMe_3$	1	77, 78, 79	77, 78, 79	
		145	145	
$AlEt_3$	1	40, 146	40	
$AlBu^i_3$	1	147	147	
Group IVA				
$SiCl_4$, $GeCl_4$	–			73
$SnCl_4$	1, 2	40, 41, 46		
	–	150, 151		
SnR_2H_2	–		81, 83, 152	
SnR_3H	–		80, 82, 83	
Sn+HCl	–			154
Group VA				
$PCl_3[NPCl_3^+Cl^-]$	–			155
PR_3	–		92, 120, 121	156
(R=alkyl, aryl)				
$SbCl_5$	1	45, 71	45	

TABLE 5 (continued)

Lewis acid [a]	n [b]	Type of study		
		Spectra	Reactions	Misc.
$BiPh_3$	–			103
Group IVB				
$TiCl_4$	2	19, 40, 41 43, 158	19, 158, 159	
	1	158, 160	160	
$TiCl_4+R_3N$	–		109, 113	
TiX_3 (X=Cl, Br)	3	19, 43	19, 158	
$TiCl_3$	3	306	113,126	306
$ZrCl_4$	2	43		
Group VB				
$VOCl_3$	–	160		150
$VOCl_2$	2	19	19	
	–		161	
VCl_4	4	160	160	
	2	160	43, 159, 160	
VX_3	3	19, 43	19,43	
(X=Cl, Br)	2		153	
	–		161	
VCl_3+R_3N	–		109,113	
$VCl_3+Mg+ROH$	–		126	
$V(acac)_3$	–		162	
VCl_2	–	161	163	
MX_5(M=Nb, Ta;	1	43, 44		
X=Cl, Br)	–	164, 165		
MX_4(M=Nb, Ta; X=Cl, Br)	2	43, 44	43	
$NbMe_2Cl_3$	1	166	166	
$TaMeCl_4$	1	166	166	
Group VIB				
$CrCl_3$	3	19, 41	167, 168	
	–	161		
$Cr(ClO_4)_3$	3		168	
$CrCl_2^+$	4		168	
CrX_2 (X=Cl, Br, I)	–	161	112	
$Cr(CO)_5$	1	42, 169	169	
$Cr(CO)_4$	2	51	51	
$Cr(CO)_2L$ (L=arene)	1	42		
$MoCl_3$	3	47	47	
	–	161		

TABLE 5 (continued)

Lewis acid [a]	n [b]	Type of study		
		Spectra	Reactions	Misc.
$MoCl_5^{2-}$	1	47	47	
$Mo(CO)_6 + PPh_3$				171
$Mo(CO)_4$	2	51	51	
$Mo(CO)_3$	3	51	51, 172	
$Mo(CO)_2$	2	174, 175	174	
$Mo(CO)_x(PPh_3)_2$ ($x = 2, 3$)	2, 1	176, 177	173, 176, 177	
$Mo(CO)_2(PBu_3)_3$	1	176	176	
$[Mo(CO)_2(PBu_3)_2]_2$	2	178		
$Mo(C_5H_5)_2$	1	89, 179	89, 179	
$MoH_2(C_5H_5)_2$	–		179	
WCl_6	–		180	
WCl_4	1		91	
$W(CO)_6 + PPh_3$	–			171
$W(CO)_5$	1	42, 51, 169, 170, 181	51, 181	
$W(CO)_4$	2	51	51	
$W(CO)_3$	3	51, 181	51, 181	
$W(C_5H_5)_2$	1	179	179	
Group VIIB				
$MnCl_2$	2			139
	1	19, 41	19	139
$MnX_2 + R_3N$ ($X = Cl, Br, I$)	–		112	
$Mn(SbCl_6)_2$	6	141	141	
$Mn(InCl_4)_2$	3	141	141	
$Mn_2(CO)_9$	1	182	182	
$Mn(C_5H_5)(CO)_2$	1	183	183	
$Re(N_2COPh)Cl_2$-$(PPh_3)_2$	1	184		
Group VIII				
$FeCl_3$	–	161	19, 126, 185	186
$Fe(acac)_3 + RNC$	–		115	
$FeCl_2 \cdot 2\ FeCl_3$	6	19, 41		
$FeCl_2$	1	19, 41		
$FeCl_2 + Mn$	–		123	
$Fe(SbCl_6)_2$	6	141	141	
$Fe(InCl_4)_2$	3	141	141	
$FeCl_2 + R_3N$	–		109, 113	
$Fe(C_5H_5)(CO)(PPh_3)^+$	1	314		
$Fe(acac)_2 + RNC$	–		115	
$Fe(CNC_6H_4Me)_5^{2+}$	1	187		

TABLE 5 (continued)

Lewis acid [a]	n [b]	Type of study		
		Spectra	Reactions	Misc.
$Fe^{2+}(Fe_x(CO)_y)^{2-}$ ($x=1$–4; $y=4$, 8, 11, 13)	1	23	23	
$Fe(bipy)R_2$	1		189	
$Fe(C_5H_5)(CO)_2^{2+}$	1	190	190	191
$Fe(C_5H_5)(CO)_2H$	–		87	
$Fe(CO)_4$	1	23, 24, 60 192, 193, 194	23, 60, 157 195, 196, 197	188, 193, 194
$Fe_2(CO)_6$	2	198		
$Fe_x(CO)_yH^-$ ($x=1$–3; $y=4$, 8, 11)	–		119	
$Fe(PF_3)_4$	1	199		
$Fe(C_7H_9)(CO)_2^+$	1	200		
$RuCl_3$	–	106		107
$Ru(NH_3)_5Cl_3$	1	201	201	
$Ru(MPh_3)_2X_3$ (M=P, As; X=Cl, Br)	1	202, 203, 204	202, 203, 204	
$RuCl_3+BiPh_3$	–		103	
$RuCl_3\cdot3(H_2O)+H_2$	–		96, 97, 98	
	–		108, 205, 206	
$RuCl_3(PPh_3)_3+H_2$	–		206, 207	
$Ru(OAc)_2OH+H_2$	–		207,208	
$Ru(acac)_3+H_2$	–		96, 99	
$Ru(OH)_3+H_2$	–		208	
$[Ru_3O(RCO_2)_6(H_2O)_3]^+$ (R=Me, Et)	–		108	
RuX_2 (X=Cl, I)	4	209	100, 209, 210	
$RuCl_2$	3	98	98	
	2	99	99	
$Ru(NH_3)_5Cl_2$	1	201	201,258	
	–	49		
$Ru(PPh_3)_2Cl_2$	2	211	96, 100, 211	
$Ru(AsPh_3)_2Cl_2$	2	202	202	
$Ru(H_2O)Cl_2$	3		100	
$RuCl_2(CO)(C_8H_{12})$	1	212	212	
$Ru(acac)_2CO$	1		101	
$RuX_2(CO)_3$ (X=Cl, Br)	1	213	213	
$Ru(bipy)_2^{2+}$	–		214	

TABLE 5 (continued)

Lewis acid [a]	n [b]	Type of study		
		Spectra	Reactions	Misc.
$[Ru(CH_2{:}CHCH_2\text{-}NH_2)(bipy)_2]^{2+}$	1		214	
$[RuCl(R)(CO)_2]_2$	2	215	215	
$RuCl(R)(CO)_2PPh_3$ ($R=C_3H_5$)	1	215	215	
$[RuCl_3CO]^-$	2	216	216	
$RuCl_2(CO)_2py$	–		96	
$Ru_2(RCO_2)_4Cl$	–		104	
$Ru(PPh_3)_2(C_5H_5)^+$	1	311		
$RuCl_2(PPh_3)_2$	2		100	
$RuCl_2(SbPh_3)_3$	–		206	
$OsHCl(CO)\text{-}\{P(C_6H_{11})_3\}_2$	1	217		
$CoX(DMG)_2$ ($X=Cl$, Br)	1	218		
$CoCl(DMG)_2py$	–		219, 220, 221	
$Co(CN)_5H^{3-}$	–		84, 222	
$Co(NH_3)_5^{3+}$	1	223	224,308	
Co(etmcp) (etmcp= $[C_5Et(Me)_4]^-$	3	313		
$CoCl_2$	1	19, 41	19	225
CoX_2+R_3N ($X=Cl$, Br, I)	–		107, 109, 113	
CoX_2+M ($X=Cl$, Br, I; $M=Mg$, Zn, Mn)	–		122, 124, 125 128, 226	
$Co(O_3SCF_3)$	–		114	
$Co(NO_3)_2$	–			139
$Co(SbCl_6)_2$	6	141	141	
$Co(InCl_4)_2$	3	141	141	
$Co(acac)_2+C_6H_{11}NC$	–		115	
$(C_5H_5)Co(C_4H_4)PPh_3$	–		227	
$(C_5H_5)CoC_2Ph_2$			228	
$Co(CN)_2(PEt_3)_2^-$	1			229
$CoH\cdot N_2(PPh_3)_2$	1		230	231
$CoMe(PPh_3)_2$	1		232	
$Co(DMG)_2^-$	–		117	
$Co(CO)_2$	1		233	
$Co_2(CO)_8$	–		119, 234	
$Co_2(CO)_8\cdot PhC{:}CH$	–		235	
$Co(P(O^iPr)_3)_3$	1	236	236	

TABLE 5 (continued)

Lewis acid [a]	n [b]	Type of study		
		Spectra	Reactions	Misc.
$Rh(PPh_3)X \cdot X'$ ($X=Cl$, Br; $X'=CN$, I)	1		237	
$Rh(NH_3)_5Cl_3$	1	238		
	–	49	90	
$RhCl_3$	3		239	
$RhCl_3+R_2PHO$	–		240	
$RhCl_2$	2		241	
RhCl	2	242	242	
$RhXH_2(PPh_3)_2$ ($X=Cl$, Br, I)	1		243	
RhL_2^+ ($L=$bipy, phen)	1	244	244	245
$RhCl(PPh_3)$	–		246, 247	
$Rh(C_8H_{12})^+$	2		312	
$Rh(C_8H_{12})P(XC_6H_4)_3^+$ ($X=F$, H, CH_3, OCH_3)	1		312	
$\{Rh(CH_2{:}CH_2)_2\}_2Cl_2$	–		248	
$Rh(C_5H_5)$	1	249	249	
$Rh(C_5H_5)(PPh_3)_3$	1	249	249	
$RhCl(PF_3)_2$	1	250	250	
$Rh(\eta^5 C_9H_7)$	2	251	251	
$Rh(C_5H_5)(CH_2{:}CH_2)$	1	252	252	
$Ir(CH_2CH_2CN)CO(PPh_3)_2$	1	88		
$IrX(CO)(MPh_3)_{2,3}$ ($X=Cl$, F, NCS, NCO; $M=P$, As)	1	76, 253, 254 255	76	
$IrL(C_8H_{12})^+$ ($L=$bipy, phen)	1	256	256	245
NiX_2 ($X=Cl$, Br, I)	2, 4	257, 258, 259 310		
$NiCl_2$	1.1, 2.2, 4	19	19	
$Ni(SbCl_6)_2$	6	141	141	
$Ni(InCl_4)_2$	3	141	141	
$Ni(CN)_2$	[c]	260		
$Ni(NO)_3$				139
NiR_2bipy	1	261, 262	261	263
$Ni(acac)_2+RNC$	–		115	

TABLE 5 (continued)

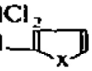
Lewis acid [a]	n [b]	Type of study		
		Spectra	Reactions	Misc.
Ni	2	18, 62, 64 264	64, 127, 129 130, 134, 265, 266, 267, 268, 269, 270	66, 271 273, 274
$Ni(PPh_3)_x$ ($x = 1, 2$)	2	62, 65	7, 62, 133	66
Ni bipy	2			274
	1	261	261	263
$Ni[P(O\text{-}o\text{-tolyl})_3]_2$	1	33, 75, 59	59, 237, 275 276	
	–			74
$Ni(CO)_4$	–		277, 278	
$PdCl_2$	–		279	
Pd  (x = O, S)	–		280	
$Pd(PPh_3)_2(OAc)_2$	–		281	
$PdBrR(PR'_3)_2$	–		282	
$Pd(PPh_3)_2$	1			283
Pd bipy	1	284	284	
$PtCl_2$	2	285	286	
PtCl(OH)	1.5	286	286	
$PtCl_2$(TMA)	1	288		
$PtCl_2$(amine) (amine = [PhMeC(H) N(Me)$CH_2]_2$)	1	315		
$Pt(CH_2{:}CH_2)Cl_2L$ ($L = Et_2NH, PPh_3$)	–		108	
$PtMe(PMe_2Ph)^{2+}$	1	289		
$Pt(PPh_3)_2$	1	63, 290, 291		283
$PtMe[(pyz)_3BH]$	1	292, 293		
$PtCF_3(PMe_2Ph)$	1	294		
Group IB				
$CuCl_2$	1	32	32	
$(CuCl_2)_2$	1	19,41	19	
$CuCl_2 + CCl_4$	–		185, 295	
$Cu(acac)_2 + RNC$	–		115, 296	
Cu_2Cl_2	2	151		
	1	61	61	
$Cu(CF_3SO_3)_2$	1, 2	297	297	
$CuBF_4$	4		298	
$CuSnCl_3$	1	97	97, 287	
$CuClO_4$	2	299	299	
$AgNO_3$	–	300		301

TABLE 5 (continued)

Lewis acid [a]	n [b]	Type of study		
		Spectra	Reactions	Misc.
$ZnCl_2$	2	19, 41, 302	19, 135	
	1	40, 302		138
	–		303	136, 137, 139, 304
$Zn(SbCl_6)_2$	6	141	141	
$Zn(InCl_4)_2$	3	141	141	
ZnX_2+R_3N ($X=CF_3CO_2$, $NCCH_2CO_2^-$, p-tolyl SO_3^-)	–	109, 111, 113		
$CdCl_2$	2	41	41	
CdX_2+R_3N ($X=CF_3CO_2$, $NCCH_2CO_2^-$, p-tolyl SO_3^-)	–		109	
Actinides				
$UO_2[(CF_3CO)_2CH]_2$	1		307	

[a] For the purpose of this tabular survey the term Lewis acid includes those compounds used as catalysts in the oligomerization of acrylonitrile. In such cases the existence of an adduct species may only be transitory and in consequence no value of n is indicated.
[b] Indicates the stoichiometry (Lewis acid) $(CH_2:CHCN)_n$.
[c] Intercalate.

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