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ORGANONITRILE COMPLEXES OF TRANSITION METALS

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CONTENTS

ABBREVIATIONS

M	metal
R	alkyl or aryl group
Ph	phenyl group
Me	methyl group
Et	ethyl group
Pr	propyl group
Bu	butyl group
Cp	cyclopentadienyl group
Depe	$Et_2PCH_2CH_2PEt_2$
Dppe	$Ph_2PCH_2CH_2PPh_2$

Diars	$o\text{-}C_6H_4(AsMe_2)_2$
Bipy	2,2′-bipyridyl
Phen	*o*-phenanthroline
En	ethylenediamine
Py	pyridine
DMG	dimethylglyoximate ion
COD	1,5-cyclooctadiene
NBD	norbornadiene
THF	tetrahydrofuran

A. INTRODUCTION

The chemistry of metal—nitrile complexes was reviewed by Walton in 1965 [1], and since that time there has been considerable interest in such complexes. That organonitriles are of interest as ligands is not surprising in view of the facts that the RC≡N: group is isoelectronic with molecular nitrogen and that organonitrile complexes can serve as convenient precursors for a wide variety of coordination compounds.

The purpose of this review is to summarize the literature which has appeared since 1965 that deals with the structural, bonding, and reactivity patterns of organonitrile complexes of transition metals. The emphasis, however, will be on the reactions which coordinated nitrile groups undergo.

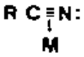
In addition to Walton's review [1], the coordination chemistry of organonitriles has also been briefly summarized in the MTP Reviews [2] and in the excellent book "The Chemistry of the Cyano Group" [3].

B. STRUCTURAL STUDIES OF NITRILE COMPLEXES

Organonitriles have two potential coordination sites, namely the nitrile—nitrogen lone pair (I) and the carbon—nitrogen triple bond (II). The majority of the nitrile complexes involve interactions of Type I [1], but side-on interactions, II, have been confirmed for a few complexes (vide infra Sect. B(ii)).

$RC{\equiv}N{:}{\rightarrow}M$

I



$R\,\underset{\substack{\downarrow\\ M}}{C{\equiv}N}{:}$

II

(i) *Complexes with end-on nitrile—metal interactions*

A list of the compounds whose structures have been determined by X-ray diffraction techniques is given in Table 1 along with selected bond distances and angles. For most compounds, the M—N—C angle is sufficiently close to 180° to suggest that the nitrile ligand is coordinated in a linear or end-on manner. In the past, non-linear metal—nitrile linkages have been attributed to the partial use of sp^2 hybrid orbitals by the nitrogen [4] and to crystal packing effects [5]. For example, it has been proposed that crystal packing effects, caused primarily by the rigid nature of the N—C—C framework, are largely

TABLE 1

Selected structural parameters for transition metal nitrile complexes

Compound	M—N—C angle (deg.)	M—N distance (Å)	N—C distance (Å)	Ref.
$[TiCl_4NCCOOC_2H_5]_2$	178.1(2)	2.240(3)	1.112(3)	12
$VO(NO_3)_3(NCCH_3)$	≈180	2.24(3)	1.17(3)	13
$VOCl_3(NCCH_3)$	175.4(1)	2.098(2)	1.137(2)	14
$NbOCl_3(NCCH_3)_2$ [a]	178.2(2) 175.9(2)	2.245(9) 2.44(2)	1.159(6) 1.12(1)	15
$NbBr_4(NCCH_3)_2$	174(9)	2.03(10)	1.09(14)	16
$WCl_4(C_2Cl_5N)(NCCCl_3)$	≈180	2.37	1.07(5)	17
$ReCl_3(PPh_3)_2(NCCH_3)$	175	2.05(3)	1.17(5)	18
$ReCl_4(NO)(NCCH_3)$	172(4)	2.07(5)	1.20(8)	10
$[AsPh_4][Re(O)Br_4(NCCH_3)]$	170(4)	2.31(6)	1.22(8)	7
$[NEt_4][ReBr_4(NO)(NCCH_3)]$	177(2)	2.153(11)	1.12(2)	11
$[Fe(NCCH_3)_6][FeCl_4]_2$	175.7(5)	2.190(10)	1.09(1)	19
$[Fe(NCC_2H_5)_5Cl][FeCl_4]_2$	≈180	2.08(av)	1.15(av)	20
$[Rh(C_2H_4)_3(NCCH_3)_2][BF_4]$	≈180	1.98(2)	1.21(av)	9
$[Ni(EtOOCC_2H_4COOEt)_2(NCCH_3)]$	178(8)	1.888(4)	1.129(6)	21
trans-$PtCl_2(NCC_6H_5)_2$	179.3(1)	1.950(15)	1.09(2)	22
$Cu(NO_3)_2(NCCH_3)_2$	175(5)	1.92(6)	1.03(7)	23
$CuCl(NCCH_3)$	172.8	2.00(2)	1.14(1)	24
$CuBr(NCCH_3)$	173.4(9)	2.00(2)	1.158(8)	25
$[Cu(NCCH_2CH_2CN)_2]ClO_4$	169.7(5)	1.987(5)	1.18(6)	5
$[Cu(NCCH_3)_4]ClO_4$	174(av)	1.98(av)	1.13(av)	26
$[Cu(C_{12}H_{20}N_2)_3][SbCl_6]_2$	168.4(av)	2.110(av)	1.134(av)	6
$CuCl(NCC_6H_5)$	175.5(6)	1.949(7)	1.087(12)	27
$CuBr(NCC_6H_5)$	172.3(5)	1.941(7)	1.087(12)	27

[a] The acetonitrile ligands are non-equivalent.

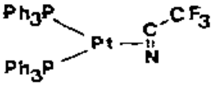
responsible for the departure of the Cu—N—C angle from linearity (169.7°) in $[Cu(NCCH_2CH_2CN)_2]ClO_4$ [5]. The same effects are considered responsible for the large C—C—C angle (114°) observed for the succinonitrile portion of this complex [5]. Similar effects may account for the angle (168.4°) observed for the Cu—N—C angle in the dodecanedinitrile complex $[Cu(C_{12}H_{20}N_2)_3]^{2+}$ [6]. The $[Re(O)Br_4(NCCH_3)]^-$ ion has a Re—N—C angle of 170°, but this deviation from linearity is probably not significant due to errors in locating the light-atom positions [7].

The C—N bond lengths of the coordinated nitriles are of interest from the standpoint that spectroscopic measurements suggest that in many cases the

C—N bond strength increases upon coordination (vide infra Sect. D(i)). From such measurements, a small but significant shortening of the C—N bond length is expected upon coordination. The C—N bond distances associated with coordinated acetonitrile are in substantial agreement with this expectation. If the equilibrium C—N distance in CH_3CN is assigned the value of 1.155 Å [8], the distances for complexes listed in Table 1 are within experimental error of this length or shorter. The long distance of 1.22 Å reported for $[Re(O)Br_4(NCCH_3)]^-$ is attributed to errors in locating the light atom positions as described before [7]. However, no explanations are given for the long C—N distances found in $[Rh(C_2H_4)_3(NCCH_3)_2]^+$ [9] and $ReCl_4(NO)(NCCH_3)$ [10]. For the latter compound, it appears that this distance is also due to errors in locating light atom positions because the C—N distance in $[ReBr_4(NO)(NCCH_3)]^-$ is accurately known to be 1.12 Å [11].

(ii) Complexes with side-on nitrile—metal interactions

In contrast to complexes with end-on coordination, side-on coordination has been confirmed for only one carbonitrile complex $Pt(PPh_3)_2(NCCF_3)$ [28] and for the cyanamide complex $[Ni(CO)(NCNC_5H_{10})]_2$ [29]. Even though the results of the complete X-ray study have not been published, it has been reported that the platinum complex has the planar arrangement shown in III [28]. The IR spectrum of III was found to display a strong band at 1734 cm^{-1}



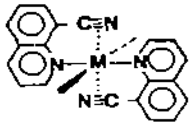
III

which was assigned to the ν(CN) band.

C. COMPLEXES PROPOSED TO CONTAIN SIDE-ON COORDINATED NITRILES

Even though side-on interactions have been confirmed for only two complexes (vide supra), such coordination has been proposed recently for several other complexes. These include the cyanamide complexes $[Ni(CO)(NCNR_2)]_2$ [30] which are analogous to the piperidine complex which has been the subject of an X-ray crystallographic study [29]. The ν(CN) bands for these $[Ni(CO)(NCNR_2)]_2$ complexes were found at lower frequencies than the bands in the free ligands and the values 2008 and 1988 cm^{-1} reported for the dimethylcyanamide and *N*-cyanopiperidine complexes, respectively. These values represent shifts upon coordination of —204 and —227 cm^{-1} in the ν(CN) bands.

Sutton and Zink [31] have recently reported studies of 8-cyanoquinoline (L) complexes of the types ML_2X_2 (M = Pd, Pt, Cu; X = Cl, Br) and $[AgL_2]$-

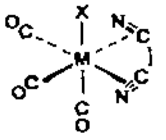


IV

NO_3 [31]. A calculation utilizing expected bond lengths indicated that in these the strongly coordinating quinoline nitrogen should hold the CN group perpendicular to the metal at a distance of ca. 2.35 Å. The ν(CN) bands in the IR spectra of the complexes were observed at slightly lower frequencies, -3 to -8 cm^{-1}, than the corresponding bands in the free ligands. It was proposed that the small shifts result from weak nitrile—metal interactions rather than from inductive effects associated with the coordination of the quinoline nitrogen. In support of this proposal, it was found that the ν(CN) of the uncoordinated nitrile group in dichlorobis(3-cyanopyridine)palladium(II) was 8 cm^{-1} higher in frequency than in the free ligand.

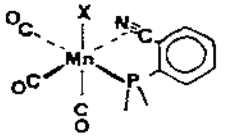
It should be noted, however, that the CN stretching frequencies of remote, uncoordinated nitrile groups in bidentate ligands have been observed to shift upon coordination of one of the donor sites to either higher or lower frequencies. For example, Walton has reported, in accord with the observation of Sutton and Zink, a small increase in the ν(CN) upon coordination of the pyridine nitrogen in complexes of the type $PdCl_2$(3-cyanopyridine)$_2$ [32]. In contrast, however, Walton has reported a decrease of 20 cm^{-1} for the analogous complex of 4-cyanopyridine [32]. Ford has also observed a decrease of 3 cm^{-1} upon coordination in the ν(CN) associated with the remote nitrile group in $[Ru(NH_3)_5[1,3\text{-}C_6H_4(CN)_2]]^{2+}$ [33]. For this last complex, however, the significance of the small shift is not easy to access in view of the fact that anion—cation effects have also been observed to cause shifts of this magnitude [33,34].

Several studies have focused on Mn(I) and Re(I) complexes of the potentially bidentate ligands malononitrile [35], succinonitrile [35], glutaronitrile [35], phthalonitrile [35], and (o-cyanophenyl)diphenylphosphine [36,37]. For these ligands the following types of complexes have been proposed, large-



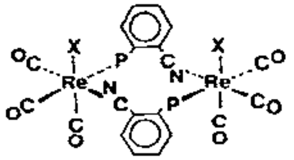
V

M=Mn; X=Cl,	malononitrile, succinonitrile
X=Br;	malononitrile, succinonitrile, glutaronitrile, phthalonitrile
M=Re, X=Cl, Br;	malononitrile, succinonitrile, glutaronitrile



VI

X=Cl, Br, I

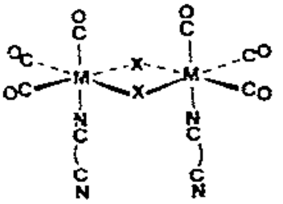


VII

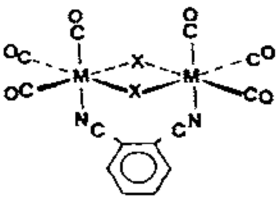
X=Cl, Br

ly on the basis of IR spectral data. The IR spectra of V—VII are reported to be similar to each other in that they display very weak or undetectable bands in the ν(CN) region (2200—2300 cm^{-1}). Bands in the ν(CO) region, e.g. at 1920 cm^{-1} for VII (X = Cl) and at 2070 for Mn(CO)$_3$(succinonitrile)Cl, have been assigned to the CN stretching vibration associated with the side-on coordinated nitriles.

The formulation of V—VII as complexes with side-on coordinated nitriles has proved to be controversial and data have been presented which indicate that the nitriles may be end-on coordinated [38—40]. In support of the end-on formulation it has been found that the Raman spectra of the Re(I) complexes display strong bands at ca. 2250 cm^{-1} which can be assigned to end-on coordinated nitrile groups. Furthermore, Dunn and Edwards have concluded from isotopic substitution experiments that the IR bands originally assigned to the ν(CN) vibration in the Mn(CO$_3$)(dinitrile)X are ν(CO) bands [38]. Hence, the following types of structures have been proposed for the complexes of type V [38,39].



VIII



IX

The formulation of Mn(CO)$_3$(dinitrile)X (previously formulated as V) as VIII requires that ν(CN) vibrations associated with both the coordinated nitrile group and the free group appear as very weak bands in the IR spectra. It is fairly well established that the ν(CN) associated with end-on coordinated nitriles may be very weak in intensity or undetectable in an IR spectrum. This intensity pattern has been reported for several complexes including Re(PPh$_3$)$_2$(CH$_3$CN)Cl$_3$ [41] which is known to contain a linear Re—N—C grouping [18], the platinum(II) complexes [Pt(L)$_2$(NCR)(CH$_3$)]$^+$ (L = PMe$_2$Ph, AsMe$_3$) [42], and [Fe(p-CH$_3$C$_6$H$_4$NC)$_5$NCCH$_3$]$^{2+}$ [43].

The IR intensity patterns of remote, uncoordinated nitrile groups are not as well documented. The absence of ν(CN) bands at or near the frequencies observed for the free ligand has been noted, however, for [Ru(NH$_3$)$_5$[1,4-C$_6$H$_4$(CN)$_2$]]$^{2+}$ [33], CpMn(CO)$_2$[1,4-C$_6$H$_4$(CN)$_2$] [44], and CpMn(CO)$_2$(NCCHCHCN) [44]. In contrast, the ν(CN) associated with the free nitrile groups in Re(CO)$_3$(PPh$_2$CH$_2$CH$_2$CN)$_2$X (X = Cl, Br) [45] and [Ru(NH$_3$)$_5$[1,3-C$_6$H$_4$(CN)$_2$]]$^{2+}$ [33] are readily observable in the IR spectra at essentially the same frequencies observed for the free ligands.

Side-on coordination has also been proposed for several additional complexes (see Table 2). For these complexes, IR spectroscopic measurements, particularily in the ν(CN) region, have been extensively utilized to determine the mode of metal—nitrile interaction. However, as discussed in this and the

TABLE 2

Transition metal complexes proposed to have side-on coordinated nitrile groups

Complex	ν(CN)	$\Delta\nu$(CN)	Ref.
$Cp_2Mo(NCR)$			46
$R = CH_3$	[a]	−494	
$R = CF_3$	[a]	−526	
$R = C_6H_5$	[a]	−489	
$(PPh_3)_4Ru(NCCH_3) \cdot CH_3CN$	1910	−344	47
$[(L_2MePt)_2 4\text{-}NCC_6F_4C(OEt)NH]^{2+}$ [b]	2141	−113	42
$Cd(NCCH_2CN)_2Cl_2$	2200	−75	48
$[Mo[C_2H_5OC(O)CN]_3]_n$	2200, 2120, 2060 2000, 1935	—	49
$[W[C_2H_5OC(O)CN]_3]_n$	2215, 2155, 2050 1995, 1902	—	49
$[Mn(CO)[C_2H_5OC(O)CN]_2]_2$	2120	−140	49
$CpMn(CO)[C_2H_5OC(O)CN]$	2220	−40	49
$Fe(CO)[C_2H_5O(CO)CN]_3$	2120	−140	49
$[(PR_3)_3Co(NCR')]_n$			50
$R = n\text{-}C_8H_{17}$, $R' = C_6H_5$	2130	−114	
$R = n\text{-}C_8H_{17}$, $R' = CH_3$	2110	−156	
$R = n\text{-}C_4H_9$, $R' = C_6H_5$	2120	−124	
$R = C_6H_5$, $R' = C_6H_5$	2100	−144	
$[M(CO)_3(Et_2NCH_2CN)]_2$			51
M = Cr	2118	−102	
M = Mo	2110	−110	
M = W	2120	−100	
$Fe(CO)_3(Et_2NCH_2CN)$	2110	−110	51
$[Mn(CO)_2(Et_2NCH_2CN)]_3$	2145, 2120	−75, −100	51
$[Cr(CO)_3(Et_2NCH_2CN)]^-$	2110	−110	51

[a] This value was not reported. [b] $L = PMe_2Ph$.

following section, structural assignments made on the basis of such measurements should be viewed with scepticism.

D. SPECTROSCOPIC PROPERTIES OF COMPLEXES WITH END-ON COORDINATED NITRILES

The discussion in the previous section indicates the important role that vibrational spectroscopy has played in the assignment of the mode of nitrile—metal interactions. Traditionally, the effect of coordination on the ν(CN) bands in the IR spectra of the nitrile complexes has been used to make the assignments. Shifts to higher frequencies have been considered characteristic of end-on coordinated nitriles and shifts to lower frequencies characteristic of side-on coordinated nitriles. Recently, however, it has become evident that end-on coordination can cause the ν(CN) to shift to either higher or lower frequency. In view of these shifts, and the important role that vibrational spectroscopy plays in bonding assignments, the recent literature which deals with IR and Raman measurements of nitrile complexes will be summarized. Some of Shriver's recent reports describing acetonitrile adducts of main-group elements will be included even though they do not deal with transition metal complexes because they provide some of the few thorough spectroscopic studies of nitrile complexes.

(i) Carbon—nitrogen stretching frequencies: ν(CN) "coordinated" > ν(CN) "free"

Shriver has studied the vibrational spectra of several acetonitrile adducts of Lewis acids including $MX_5 \cdot NCCH_3$ (M = As, X = F [52], M = Sb, X = Cl [52], M = Sb, X = F [53]) and $BX_3 \cdot NCCH_3$ (X = F [54], Cl [55], Br [55]). For these end-on coordinated acetonitrile complexes, Shriver has noted that the most obvious change in the IR bands is an increase in the ν(CN) frequency. For the $BX_3 \cdot NCCH_3$ adducts, the shifts were observed to be about +100 cm^{-1} which is significantly larger than the shift of +61 cm^{-1} observed for $SbF_5 \cdot NCCH_3$. In regard to these shifts, Shriver has pointed out that the large, positive $\Delta\nu$(CN) observed for the $BX_3 \cdot NCCH_3$ adducts does not necessarily indicate that the BX_3 centers are stronger acids than SbF_5 and that the $\Delta\nu$(CN) may not be directly related to acid strengths [53].

In addition to the increase in the ν(CN) upon end-on coordination of CH_3CN, increases have also been observed for the CCN deformation band, the CC stretch, and for some other combination bands [52—57]. For example, the CC stretching frequency for CH_3CN was observed to increase by ca. 30 cm^{-1} upon coordination in $SbCl_5NCCH_3$ [52] and in *fac*-$RhCl_3(NCCH_3)_3$ [57].

The increase in the ν(CN) upon coordination has been attributed to an increase in the CN stretching force constant which is due to an increase in the strength of the CN σ-bond [58,59]. The increase upon coordination in the force constant associated with the CN bond has been confirmed for $BF_3 \cdot NCCH_3$ [54], $SbX_5 \cdot NCCH_3$ (X = Cl, F) [52], and $AsF_5 \cdot NCCH_3$ [52] for which the force constants were calculated to be 18.0—18.8 mdyn Å^{-1} compared to 17.4 mdyn Å^{-1} for free CH_3CN.

The IR spectra of acetonitrile complexes frequently display two bands in the ν(CN) region. One is the ν(CN) band and the other a combination band resulting from the symmetrical CH_3 deformation and the C—C stretch which borrows its intensity from the ν(CN) band [60]. The assignment of the combination band can be accomplished by comparing the spectrum of the CH_3CN adduct to that of the CD_3CN adduct [54]. It should also be noted that the combination band and the ν(CN) band are subject to Fermi resonance coupling so it is frequently necessary to correct the observed frequencies to account for it.

Walton has assigned bands to the ν(CN) and combination modes in the spectra of both the *cis* and *trans* isomers of $Re(Cl)_4(CH_3CN)_2$ [61]. For the *trans* compound a single strong IR band was observed at 2285 cm^{-1} which was assigned to the ν(CN) band and a medium intensity band was observed at 2315 cm^{-1} with a shoulder at 2305 cm^{-1} which was assigned to the combination band. For the *cis* isomer, bands of comparable intensities were observed at 2284 cm^{-1} and 2310 cm^{-1} with shoulders at 2290 and 2320 cm^{-1}. Again the lower energy band was assigned to the ν(CN) vibration. The ratio of the intensity of the ν(CN) band to that of the combination band was found to be a major spectroscopic difference for the two isomers.

Dunn and Edwards have reported that the IR spectra of $M_2(CO)_6(NCCH_3)_2X_2$ (M = Mn, Re; X = Cl, Br, I) display two bands in the ν(CN) region [62]. For example, bands at 2322 and 2298 cm^{-1} are reported for $Re_2(CO)_6(NCCH_3)_2Cl_2$, but for this and the related complexes, the ν(CN) frequency has been assigned to the higher energy band.

(ii) Carbon—nitrogen stretching frequencies: ν(CN) "coordinated" < ν(CN) "free"

Strohmeier and Guttenberger reported the first examples of nitrile complexes assigned end-on coordinated formulations which displayed ν(CN) bands in their IR spectra at frequencies lower than those of the free nitriles [63,64]. Shifts of ca. −35 cm^{-1} were observed for the benzonitrile and acrylonitrile complexes of the type $ARENECr(CO)_2NCR$ (ARENE = $1,3,5\text{-}C_6H_3(CH_3)_3$, $C_6(CH_3)_6$).

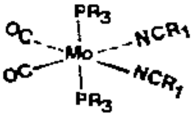
Several additional nitrile complexes of group VIB metals which fit into this category have also been reported. Included are the mixed nitrile—molecular nitrogen complexes obtained by the following reaction [65]. For these complexes the largest shifts in the ν(CN)

$$trans\text{-}Mo(N_2)_2(Dppe)_2 + RCN \xrightarrow{C_6H_5CH_3} trans\text{-}Mo(N_2)(NCR)(Dppe)_2 + N_2$$

$RCN{=}CH_3CN$, C_2H_5CN, C_6H_5CN, $4\text{-}CH_3OC_6H_4CN$, $4\text{-}NH_2C_6H_4CN$,
$4\text{-}CH_3C_6H_4CN$, $4\text{-}ClC_6H_4CN$, $4\text{-}CH_3C(O)C_6H_4CN$,
$2\text{-}CH_3C_6H_4CN$, $\frac{1}{2}\,[1,4\text{-}C_6H_4(CN)_2]$

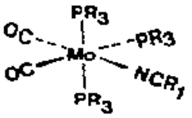
bands were observed for the complexes containing benzonitriles with electron-withdrawing substituents. Thus, a shift of −125 cm^{-1} was observed for the $4\text{-}CH_3C(O)C_6H_4CN$ complex while a shift of only −42 cm^{-1} was observed for the CH_3CN complex.

Tom Dieck and co-workers have reported over sixty nitrile complexes of Types X, XI and XII for which ν(CN) shifts from −102 to +11 cm^{-1} were observed [66,67]. Some of the typical ν(CN) frequencies are summarized in Table 3. The IR spectra of these complexes are reported to be very solvent dependent. For example, the spectrum of $Mo[P(n\text{-}C_4H_9)_3]_2(CO)_3NCC_6H_5$ displays bands at 2182 and 2159 cm^{-1} when recorded in nujol and at 2206



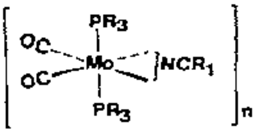
X

R = C_6H_5, n-C_4H_9
R_1 = (e.g.) C_6H_5, 4-$CH_3C_6H_4$, 4-ClC_6H_4, C(Ph)HCH



XI

R = n-C_4H_9
R_1 = (See Type X)



XII

R = C_6H_5, n-C_4H_9
R_1 = CH_2CH, 1,2-, 1,3-, and 1,4-C_6H_4CN

and 2202 cm^{-1} when recorded in benzonitrile. The structures of the complexes of type XII are not known with certainty. Dimeric formulations are favored, however, for the 1,3- and 1,4-$C_6H_4(CN)_2$ complexes, while the structures of the acrylonitrile and phthalonitrile complexes are unknown.

The manganese(I) complexes $CpMn(CO)_2NCR$ in which the nitrile is benzonitrile, a substituted benzonitrile, fumaronitrile, or cinnamylnitrile have been thoroughly studied and their IR spectra display negative $\Delta\nu(CN)$ [44,68]. Shifts of −11 and −43 cm^{-1} were reported for the NCC_6H_5 and NCC_6F_5 complexes, respectively.

Complexes of the iron-group metals have provided the most examples of shifts of this type. In particular, a large number of ruthenium complexes have been reported which belong to this category. The $[Ru(NH_3)_5NCR]^{2+}$ complexes, which are analogs of the molecular nitrogen complex $[Ru(NH_3)_5N_2]^{2+}$, have been thoroughly studied largely through the efforts of Ford [33, 69—72]. In fact, he recognized that negative shifts in $\nu(CN)$ bands are generally observed for nitrile complexes in which the nitrile occupies a site that can

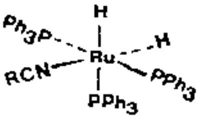
TABLE 3

IR data for Mo complexes of types X and XI

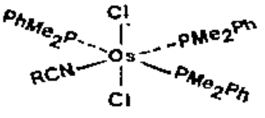
Complex type	PR_3	R_1CN	$\nu(CN)$ (nujol)	$\Delta\nu(CN)$
X	PPh_3	CH_3CN	2265	+13
X	P(n-Bu)$_3$	CH_3CN	2249	−3
X	P(n-Bu)$_3$	C_6H_5CN	2197, 2185	−33, −45
X	PPh_3	4-$CH_3C_6H_4CN$	2213, 2208	−18, −23
X	P(n-Bu)$_3$	4-$CH_3C_6H_4CN$	2204, 2189	−27, −42
XI	P(n-Bu)$_3$	CH_3CN	2231	−21
XI	P(n-Bu)$_3$	C_6H_5CN	2167	−63

coordinate molecular nitrogen [33]. For these [Ru(NH$_3$)$_5$NCR]$^{2+}$ complexes the largest shifts were observed for complexes containing substituted benzonitriles in which the substituents are electron-withdrawing groups. Thus, a shift of −59 cm^{-1} was observed for the 4-cyanobenzoic acid complex but a shift of only −23 cm^{-1} was observed for the 4-methoxybenzonitrile complex [33]. In contrast to the Ru(II) complexes, the isoelectronic [Rh(NH$_3$)$_5$NCR]$^{3+}$ complexes were found to display ν(CN) bands at frequencies higher than those of the free nitrile [33,73]. The chemical and spectroscopic properties of many of the Ru(II)—nitrile complexes have been included in a review [74] and, consequently, they will not be summarized herein.

Similar shifts for the ν(CN) bands have also been reported for *cis*- and [*trans*-Ru(NH$_3$)$_4$(NCR)$_2$]$^{2+}$ (R=C_6H_5, C_6F_5) [33], [Ru(NH$_2$R)$_5$NCR$_1$]$^{2+}$ (R=CH_3, *n*-C_3H_7, *n*-C_4H_9, *i*-C_4H_9, *i*-C_5H_{11}; R$_1$=C_6H_5) [75], [CpRu(PPh$_3$)$_2$-NCCH$_3$]$^+$ [76], Ru(H)$_2$(PPh$_3$)$_3$NCR (R=CH_3, C_6H_5) [77,78], and RuCl$_2$(L)$_2$-(NCC$_6$H$_5$)$_2$ (L=CO, phosphine, amine) [79]. Typical shifts are represented by the values of −37 and −5 cm^{-1} observed for the C_6H_5CN and CH_3CN complexes of Ru(H)$_2$(PPh$_3$)$_3$NCR, XIII [77,78].



XIII



XIV

Shifts of −40 and −35 cm^{-1} (benzene and chloroform solutions, respectively) have been reported for the ν(CN) in the benzonitrile complex XIV [80]. In contrast, the spectrum of the analogous CH_3CN complex was found to display a ν(CN) band at 2280 cm^{-1} which represents an increase of 26 cm^{-1} [80].

Several nitrile analogs of molecular nitrogen complexes of the iron-group metals have been reported and, as noted by Ford [33], shifts to lower frequency are observed for the ν(CN) bands. Included are [*trans*-M(H)(NCR)-(Depe)$_2$]$^+$ (M = Fe, Ru, Os) [81], [*trans*-Fe(H)(NCR)(Dppe)$_2$]$^+$ [82], [*trans*-Fe(NCR)$_2$(Depe)$_2$]$^{2+}$ [83], and [*trans*-Fe(Cl)(NCR)(Depe)$_2$]$^+$ [83]. These complexes are summarized in Table 4.

Nitrile complexes of cobalt, iridium, and nickel have been reported which provide negative $\Delta\nu$(CN) values. The propionitrile and acetonitrile complexes Co(H)(PPh$_3$)$_3$NCR [84], which are analogs of Co(H)(PPh$_3$)$_3$N$_2$, yield shifts of ca. −45 cm^{-1}. The iridium complexes Ir(H)(Cl)$_2$(PPh$_3$)$_2$NCR (NCR = benzonitrile or substituted benzonitrile) [85] and Ni[P(O-*o*-$C_6H_4CH_3$)$_3$]$_3$NCC$_6$H$_5$ [86] also yield negative $\Delta\nu$(CN) values.

It has been proposed that the decrease of the ν(CN) upon coordination is due to a decreased CN bond order caused by π-bonding between the metal *d* orbitals and the π^* orbitals of the CN group [33]. In addition to the evidence cited immediately below, the rates of hydrolysis observed for the [Ru(NH$_3$)$_5$-NCR]$^{2+}$ complexes are also in accord with this π-bonding proposal. This evidence is discussed in Sect. F(ii).

TABLE 4

Complexes of the types [*trans*-M(X)(NCR)(L—L)$_2$][anion] [a]

M	X	L—L	NCR	ν(CN)	$\Delta\nu$(CN)	Ref.
Fe	H	Depe	C_6H_5CN	2168	−64	81
Ru	H	Depe	C_6H_5CN	2221	−11	81
Os	H	Depe	C_6H_5CN	2196	−36	81
Fe	H	Depe	CH_3CN	2228	−26	81
Fe	H	Dppe	CH_3CN	2250	−4	82
Fe*	H	Dppe	CH_3CN	2250	−4	82
Fe	H	Dppe	C_6H_5CN	2205	−26	82
Fe	Cl	Depe	CH_3CN	2242	−12	83
Fe	Cl	Depe	C_6H_5CN	2179	−52	83
Fe	Cl	Depe	1,2-$C_6H_5(CN)_2$	2170, 2230 [b]	−60, 0	83
Fe	Cl	Depe	$NCCH_2CN$	2157, 2224 [b,c]	−121, −54	83
Fe	$NCCH_3$	Depe	$NCCH_3$	2254	0	83
Fe	$NCCH_2C(O)CH_3$	Depe	$NCCH_2CO_2CH_3$	2255	−1	83
Fe	$NCCH_2C_6H_5$	Depe	$NCCH_2C_6H_5$	[d]		83
Fe	$NCCH_2CH_2CN$	Depe	$NCCH_2CH_2CN$	2222, 2236	−35, −21	83

[a] All are BPh_4^- salts except the [Fe(H)(NCCH$_3$)(Dppe)$_2$]$^+$ ion which is a ClO_4^- salt; it is marked with an asterisk by the Fe.

[b] Assigned to the free nitrile group.

[c] Note the large negative shift (−54 cm^{-1}) for the nitrile group which is presumably uncoordinated.

[d] No detectable ν(CN) band was observed in the IR spectrum.

The ring nitrogens in the nitrile coordinated cyanopyridine complexes, [Ru(NH$_3$)$_5$NCC$_5$H$_4$N]$^{2+}$, were found to be more basic than in the free cyanopyridine even though the complex is positively charged [70,74]. This basicity pattern is consistent with the delocalization of the positive charge on the protonated ring nitrogen through the metal—nitrile π-system [70]. Furthermore, protonation of the remote ring nitrogen lowers the ν(CN) another 29 cm^{-1} [70]. This shift is in accord with the π-bonding proposal and suggests that protonation increases the π-delocalization.

The electronic spectra of many of these complexes have been recorded and bands are observable which have been assigned to metal-to-ligand charge-transfer absorptions [66,68,74,87]. Thus, an intense band is observed at 376 nm for [Ru(NH$_3$)$_5$NCC$_6$H$_5$]$^{2+}$ which has been assigned to the Ru—nitrile charge-transfer [33]. In contrast, similar bands are not obtained for the isoelectronic species [Rh(NH$_3$)$_5$NCC$_6$H$_5$]$^{3+}$ for which the IR spectra show ν(CN) bands at higher frequencies than the free ligand [73].

In addition to the evidence cited above, other features of the IR spectra of these complexes have been proposed to be in accord with the π-bonding proposal. It was found, for example, that the shifts in the ν(CN) paralleled the electron density on the metal for the $Mo(CO)_2(PR_3)_2(NCR)_2$ complexes (X) [66]. Larger negative shifts were found for the $P(n\text{-}C_4H_9)_3$ complexes than for the $P(C_6H_5)_3$ complexes which suggests a greater amount of π-bonding for the $P(n\text{-}C_4H_9)_3$ containing complexes which is in agreement with the relative donor abilities of the two phosphines. Also, the IR spectra of both [*cis*-$Ru(NH_3)_4$-$(NCR_2]^{2+}$ [38] and $Mo(CO)_2(PR_3)_2(NCR)_2$ [66], in which NCR is for example benzonitrile, showed two well separated ν(CN) bands indicative of strong coupling between the two nitrile ligands. The coupling, which has been attributed to the π interaction [66], is not evident in the spectra of complexes such as

TABLE 5

Metal—nitrogen stretching frequencies of selected nitrile complexes

Complex	ν(MN) cm^{-1}		
	IR	Raman	Ref.
AsF_5NCMe	281	270	52
$SbCl_5NCMe$	232	222	52
SbF_5NCMe		277	52, 53
MX_5NCR	220—245		92
M = Nb, Ta; X = Cl, Br; R = CH_3, CD_3, C_2H_5			
$V(O)(NO_3)_3NCMe$	407	404	93
$[M(NCMe)_6]^{2+}$	237—315		94
M = Mn, Fe, Co, Ni, Cu			
$[M(NCMe)_4]^{2+}$	163—444		94
M = Cu, Ag, Pd			
$Cr(CO)_3(NCMe)_3$	552, 495		90
$Mo(CO)_3(NCMe)_3$	533, 481		90
$W(CO)_3(NCMe)_3$	538, 481		90
$M_2(CO)_6X_2(NCMe)_2$	210—234		62
M = Mn, Re; X = Cl, Br, I			
$CoX(DMG)NCR$	435—446		95
X = Cl, Br, I; R = Me, CH_2CH			
cis- and *trans*-$RhCl_3(NCMe)_3$	456		57
[*trans*-$RhCl_4(NCMe)_2]^-$	457		57
$[RhCl_5(NCMe)]^{2-}$	429		57
cis-$PtCl_2(NCPh)_2$	109, 104, 100		89
cis-$PtCl_2(NCMe)_2$	120, 100	124	89
cis-$PtBr_2(NCMe)_2$	116, 95	117, 104	89
trans-$PdCl_2(NCPh)_2$	104	92	89
trans-$PdBr_2(NCPh)_2$		90	89
trans-$PdCl_2(NCMe)_2$	125		89
trans-$PdBr_2(NCMe)_2$	117	107	89

cis-$SnCl_4(NCR)_2$ [1] and *fac*-$Re(CO)_3(NCC_6H_5)_2Br$ [88] which show positive $\Delta\nu(CN)$ values.

Results from proton NMR studies of the $[Ru(NH_3)_5NCR]^{2+}$ complexes have been interpreted in terms of the π-bonding proposal [72]. It was observed for example, that coordination to Ru(II) causes shielding of the *meta* and *para* protons of benzonitrile. In contrast, coordination to the isoelectronic $[Rh(NH_3)_5]^{3+}$ metal center caused deshielding of these protons. The shielding at the *meta* and *para* sites is rationalized in terms of increased electron density due to metal-to-ligand π-donation.

(iii) Metal—nitrogen stretching frequencies

Reports of $\nu(MN)$ assignments for transition-metal nitrile complexes are not very numerous compared to the large number of these complexes that have been isolated. Moreover, the values that have been reported vary from ca. 100 cm^{-1} for *trans*-$PdX_2(NCPh)_2$ (X = Cl, Br) [89] to ca. 525 cm^{-1} for $M(CO)_3(NCMe)_3$ (M = Cr, Mo, W) [90]. This wide range, and the fact that the $\nu(MN)$ bands can be difficult to detect [90,91], contribute to uncertainties in assignments. Most authors, however, have recognized these uncertainties and have made only tentative assignments.

There are, however, some excellent spectroscopic studies of nitrile complexes which can be cited. Foremost are the aforementioned studies by Shriver of $MX_5(NCMe)$ (M = As, Sb; X = F, Cl) [52,53]. For these complexes, bands appearing from 222 to 281 cm^{-1} have been assigned to the $\nu(MN)$ frequencies (see Table 5). It should be noted that the $\nu(SbN)$ band for $SbF_5(NCMe)$ was originally assigned to a band appearing at 671 cm^{-1} [52], but the assignment was subsequently changed on the basis of additional data [53]. This gives some indication of the difficulties encountered in determining assignments even with thorough IR and Raman measurements.

Representative examples of nitrile complexes for which metal—nitrogen stretching assignments have been made along with the assigned band positions are presented in Table 5.

E. LIGAND PROPERTIES OF NITRILES

The ligand properties of organonitriles can be discussed only for end-on coordinated complexes in view of the fact that few examples of well characterized side-on coordinated complexes are known. In this regard, it should be noted that the basicity of the nitrogen lone pair has been the center of considerable research and the topic has been reviewed [96].

Nitriles are generally considered to be relatively moderate σ-donors and π-acceptors toward transition metals. Mossbauer studies indicate that this is the case for complexes of the types $[$*trans*-$M(H)L(Depe)_2]^+$ (M = Fe, Ru, Os) and the following order has been determined for the σ-donor and π-acceptor abilities of various ligands including acetonitrile and benzonitrile [97].

$$CO > 4\text{-}CH_3OC_6H_4NC > (CH_3)_3CNC > P(OCH_3)_3 \sim P(OC_6H_5)_3 > N_2 \sim NCC_6H_5 > CH_3CN$$

It has been postulated, however, that the σ-donor properties are more important than the π-acceptor properties in accounting for differences in the ligand properties of different nitriles in the [*trans*-$Fe(H)(NCR)(Depe)_2]^+$ system [83].

Mossbauer studies of $[Ru(NH_3)_5L]^{2+}$ (L = neutral, 2 electron-donor ligands) have been reported and the following order of π-acceptor character determined from the isomer shift data [98]. An increase of 0.1 mm s^{-1} in the isomer shift of $[Ru(NH_3)_5NCR]^{2+}$ over $[Ru(NH_3)_6]^{2+}$

$$NO^+ >> CO > SO_2 > N_2 > CH_3CN \sim C_6H_5CN > En > Py \sim NH_3$$

was observed and considered indicative of the fact that nitriles are better π-acceptors than ammonia. The isomer shifts of both the CH_3CN and C_6H_5CN complexes were found to be —0.82 which suggests that both have similar π-acceptor capabilities. Infrared studies, however, suggest that benzonitrile is a better π-acceptor than acetonitrile [33].

A ^{55}Mn NQR study of $CpMn(CO)_2L$ has provided the following ordering of ligands from $\nu(\pm \frac{5}{2} \rightleftharpoons \pm \frac{3}{2})$ data [99]. For the phosphorus

$$\begin{array}{c} CH_3CN > C_6H_5CN > Py > \text{piperidine} \\ \xrightarrow{\hspace{3em}\sigma\text{-donor strength}\hspace{3em}} \\ \xleftarrow{\hspace{3em}\pi\text{-acceptor strength}\hspace{3em}} \\ P(OPh)_3 > PPh_3 > P(n\text{-}C_4H_9)_3 > PMe_3 \end{array}$$

donors the ordering was observed to follow the general order expected for the donor—acceptor characteristics. For the nitrogen donors, however, it should be noted that the ordering suggests that CH_3CN is a weaker donor and/or better acceptor than C_6H_5CN which may not be the case [33,66].

The results from a ^{35}Cl NQR study of some d^8 transition metal complexes including *trans*-L_2PdCl_2 complexes have been reported. For these palladium complexes the charge on the chlorine atoms was found to increase as shown below [100]. The results were proposed to be indicative

$$PhCN < EtCN < P(n\text{-}C_4H_9)_3 < As(n\text{-}C_4H_9)_3 < Py < \text{piperidine}$$

of the relative donor abilities of the ligands. As expected, the donor abilities of propionitrile is greater than that of benzonitrile.

Acetonitrile has been included in the ligands evaluated using Cotton—Kraihanzel force constant methods on the IR spectra of $M(CO)_5L$ and $M(CO)_4L_2$ (M = Cr, Mo, W). From CO force constants Cotton determined that CH_3CN functioned as a weak π-acceptor, and that the $M{=}N^+{=}C^-$ and $M^-{-}N^+{\equiv}C^-$ forms could be assigned relative weights of 0.05 and 0.95, respectively [101]. Graham, on the other hand, has applied his method of separating inductive and mesomeric effects to $M(CO)_5NCCH_3$ and concluded that CH_3CN is a relatively poor σ-donor and a poorer π-acceptor than cyclohexylamine [102]. Brown and Dobson, however, have treated the spectrum of $W(CO)_5NCCH_3$ utilizing a revised version of Graham's method and determined that CH_3CN is a better π-acceptor than cyclohexylamine [103]. The ordering and π-parameters reported by Brown and Dobson are shown below.

$$CO(0.64) > P(OPh)_3(0.38) > PPh_3(0.19) \sim P(n\text{-}C_4H_9)_3(0.19) > CH_3CN(0.04)$$
$$> C_6H_{11}NH_2(0.00) \sim C_6H_6NH_2(0.00)$$

Tungsten—acetonitrile bond energies of $W(CO)_{6-n}(CH_3CN)_n$ ($n = 1, 2, 3$) have been calculated utilizing differential scanning calorimetric data from the following substitution reactions [104]. For all three

$$W(CO)_{6-n}(CH_3CN)_n + nCO \rightarrow W(CO)_6 + nCH_3CN$$

complexes the bond energies were found to be approximately 45 kcal mol^{-1} which is comparable to the W—CO bond energy.

For the $[trans\text{-}Pt(CH_3)(NCR)L_2]^+$ ($L = AsMe_3, PMe_2Ph$) complexes in which the nitrile is a *para*-substituted benzonitrile it has been observed that the ν(CN) decreases as the electron-withdrawing ability of the substituent increases [42]. This trend has been considered consistent with a $d\pi$—π^* overlap which increases as the energy of the π^* orbitals decreases [44]. However, the magnitude of the J_{PtCH}, ca. 80 Hz, in these complexes was found to change little as the *para* substituent changed. From this coupling data it was concluded that nitriles are relatively weak donors and that the donating abilities of the substituted benzonitriles are similar.

The platinum complexes $[trans\text{-}Pt(R)L_2L']^+$, $[fac\text{-}Pt(Me)_3(AsMe_3)_2L']^+$, and $[trans\text{-}Pt(Me)_2(PMe_2Ph)_2L'_2]^{2+}$ ($L = AsMe_3, PMe_2Ph$; $R = Me, Ph$; L' = neutral 2-electron ligands including $4\text{-}MeOC_6H_4CN$), have been the center of *trans*-effect studies based on carbon-13 NMR measurements [105—107]. The results from these studies are substantially in accord with the theory that the magnitude of the *trans*-effect caused by L′ is directly related to the hybridization in the Pt—L′ and Pt—R σ-orbitals [105—107]. The one-bond platinum—carbon coupling constants, $^1J_{PtR}$, are sensitive to the hybridization and these data have been used to determine the following *trans*-effect order. This order is similar to those determined by

$$\text{carbene} > CO \approx \text{isocyanide} > \text{arsine} > \text{nitrile}$$

other methods [108].

The most prominent ligand feature of organonitriles in transition metal complexes is the ease with which they can be replaced by other ligands. This has been the basis for well known synthetic procedures including the preparation of olefin derivatives of palladium and molybdenum from $Pd(Cl)_2(NCC_6H_5)_2$ [109] and $Mo(CO)_3(NCCH_3)_3$ [110].

Ease of replacement of coordinated nitriles has been noted, for example, by Treichel for [*trans*-Pt(NCCH$_3$)(CNCH$_3$)(PPh$_3$)$_2$]$^+$ in which the CH$_3$CN can be replaced by Me$_3$N, Py, PPh$_3$, Et$_3$P, (MeO)$_3$P, Me$_2$S, MeNC, I$^-$, Cl$^-$, CN$^-$, N$_3^-$, NO$_2^-$ and OH$^-$ [111]. Similarly, the acetonitrile in the manganese and rhenium complexes [M(CO)$_5$NCCH$_3$]$^+$, [M(CO)$_3$(NCCH$_3$)$_3$]$^+$, and [M(CO)$_x$L$_{5-x}$(NCCH$_3$)]$^+$ can be replaced [112,113], and the pentacarbonyl complexes have proved to be convenient starting materials for complexes of the type [M(CO)$_5$L]$^+$ [113].

$$[\mathrm{M(CO)_5NCCH_3}]^+ + \mathrm{L} \rightarrow [\mathrm{M(CO)_5L}]^+ + \mathrm{NCCH_3}$$

L = P(OPh)$_3$, PPh$_3$, PMe$_2$Ph, C$_5$H$_5$N

Organonitrile derivatives of transition and actinide metal halides have continued to receive a considerable amount of attention since Walton's review [1] and such complexes provide convenient starting materials for the corresponding hexahalogeno salts. Thus, MX$_4$(NCCH$_3$)$_2$ (M = Th, Pa, U, Zr), MX$_5$(NCCH$_3$) (M = Nb, Ta), and PaBr$_5$(NCCH$_3$)$_3$ readily react with quaternary ammonium halides to yield the [MX$_6$]$^{n-}$ salts [114].

Several complexes containing more than one acetonitrile have been reported for which there is a difference in the labilities of the CH$_3$CN ligands [115—118]. The ^{1}H NMR spectrum of [C$_3$F$_7$Fe(CO)$_2$(NCCH$_3$)$_3$]$^+$ is reported to display two signals at τ 7.51 and 7.56 with relative intensities of 2 and 1, respectively, and these are assigned to the CH$_3$ resonances [115]. The unique CH$_3$CN ligand is much more labile than the other two and it rapidly exchanges with CD$_3$CN at ambient temperature. In accord, it is also reported that the unique CH$_3$CN ligand is more readily replaced by Lewis bases than the other two [115]. Thus, reaction of the complex with an excess of ligand was found to yield only the monosubstituted derivative. In fact, it is reported that further

$$[\mathrm{C_3F_7Fe(CO)_2(NCCH_3)_3}]^+ \xrightarrow[40-50\%]{\mathrm{L}} [\mathrm{C_3F_7Fe(CO)_2(NCCH_3)_2L}]^+ + \mathrm{CH_3CN}$$

L = PPh$_3$, AsPh$_3$, P(OMe)$_3$, P(OEt)$_3$, P(OPh)$_3$

replacement of the CH$_3$CN groups could not be accomplished even under vigorous reaction conditions.

It is also reported that the complexes [M(H)(CO)(NCCH$_3$)$_2$(PPh$_3$)$_2$]$^+$ (M = Ru, Os) [116] contain acetonitrile ligands of differing labilities. Thus, the [M(H)(CO)(NCCH$_3$)$_2$(PPh$_3$)$_2$]$^+$ complexes are reported to be verstile synthetic intermediates because one CH$_3$CN group is more readily replaced than the other. For example, reaction of the complex with an excess of CO under mild conditions followed by PPh$_3$ yields [M(H)(CO)$_2$(PPh$_3$)$_3$]$^+$ rather than [M(H)(CO)$_3$(PPh$_3$)$_2$]$^+$ [116].

Lewis and co-workers have reported several acetonitrile complexes of ruthenium and osmium which contain non-equivalent CH$_3$CN groups [117]. The NMR spectra of [*cis*-M(allyl)(diene)(NCCH$_3$)$_2$]$^+$ (M = Ru, allyl = η^3-C$_3$H$_5$, η^3-(CH$_3$)CHCHCH$_2$, diene = NBD, COD; M = Os, allyl = η^3-C$_3$H$_5$, diene = COD), [*cis*-Ru(diene)(L-L)(NCCH$_3$)$_2$]$^{2+}$ ((diene)(L—L) = NBD-Bipy, NBD-Phen, NBD-Diars, COD-Bipy), $[M(diene)(NCCH_3)_4]^{2+}$ (M = Ru, diene = NBD, COD; M = Os, diene = COD), and $[Ru(L—L)(NCCH_3)_4]^{2+}$(L—L = Bipy, Phen, Diars) display two resonances due to non-equivalent CH_3CN groups. For example, resonances at τ 7.49 and 7.90 are observed for the $[Ru(NBD)(\eta^3\text{-}C_3H_5)(NCCH_3)_2]^+$ complex. Exchange studies utilizing CD_3CN indicate that the CH_3CN groups *trans* to the chelating ligands in the $[Ru(L—L)(NCCH_3)_4]^{2+}$ and $[Ru(diene)(NCCH_3)_4]^{2+}$ complexes exchange more rapidly with the solvent than those that are mutually *trans*. Two of the acetonitrile ligands in $[cis\text{-}M(NO)_2(NCCH_3)_4]^{2+}$ (M = Mo, W), which are structurally related to the ruthenium complexes, have also been observed to be more labile than the other two [118]. The addition of CD_3CN to a CH_3NO_2 solution of the tungsten-containing complex at 25° causes one of the two signals in the NMR spectrum to disappear after ca. 1 h. It is assumed that the two ligands *trans* to the NO groups are the more labile.

Even though coordinated nitriles can usually be replaced by phosphines and phosphites, it has been reported that nitriles can compete for coordination sites with P(III) donor ligands in the hydride-containing complexes $Ru(H)_2L_4$ (L = $PMePh_2$) [119] and $Co(H)L'_4$ (L′ = triarylphosphite) [120]. Benzonitrile was found to compete effectively with the phosphine for the coordination site which

$$Ru(H)_2L_4 \rightleftharpoons Ru(H)_2L_3 + L \xrightarrow[30-66^\circ]{C_6H_5CN} Ru(H)_2L_3(NCC_6H_5)$$

results from the dissociation of $Ru(H)_2L_4$ (also see complex XIII). For the cobalt complexes, triphenylphosphite, L′, readily displaced CH_3CN from $Co(H)L'_3(NCCH_3)$, but, under similar conditions, the bulky tri-*o*-tolylphosphite, L″, did not displace CH_3CN from $Co(H)L''_3$ $(NCCH_3)$. These results have been accounted for in terms of the steric requirements of the P(III) donor ligands and the nitriles [119,120], and they emphasize the small steric requirements of end-on coordinated nitriles.

Benzonitrile and acetonitrile have been ranked with other ligands as shown in the following list. The list presumably describes the order

$$CO > CH_3CN \approx C_6H_5CN > NH_3 > Py > N_2 > Me_2CO > THF$$

in which ligands can displace each other from $[trans\text{-}Fe(H)L(Dppe)_2]^+$ [82]. That acetonitrile and benzonitrile rank above pyridine is rather surprising, but it should be noted that the nitrile complexes of this type do afford IR spectra in which the ν(CN) bands are shifted to lower frequencies.

F. REACTIONS OF COORDINATED NITRILES

(i) Reactions with alcohols, thiols, ammonia, and amines

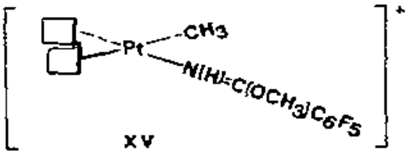
Clark and Manzer have studied the reactions of $[trans\text{-}Pt(CH_3)ClL_2]$ (L = PMe_2Ph, $AsMe_3$) [42] and $[trans\text{-}Pt(CF_3)Cl(PMe_2Ph)_2]$[121] with AgX (X = BF_4^-, SbF_6^-, PF_6^-) in the presence of nitriles. With nitriles such as 4-

$CH_3OC_6H_4CN$ the corresponding [*trans*-$Pt(CX_3)L_2NCR]^+$ complexes were obtained. However, when pentafluorobenzonitrile and 2,3,5,6-tetrafluoroterephthalonitrile were used with $AgBF_4$ in the presence of alcohols (e.g., CH_3OH, C_2H_5OH, *n*-C_3H_7OH) imino—ether complexes could be isolated. It was postulated that these facile reactions proceed via nucleophilic attack of the alcohol on a side-on

$$Pt(CH_3)ClL_2 \xrightarrow[RCN]{AgBF_4.R_1OH} AgCl + [Pt(CH_3)L_2N(H) = C(OR_1)R]BF_4$$

coordinated nitrile group [42,121].

Manzer has also reported that the reaction of $CODPt(CH_3)Cl$ with $AgPF_6$ in methanol in the presence of C_6F_5CN yields the corresponding imino—ether complex [122]. Again, it was proposed that the reaction proceeds via attack



XV

upon a side-on coordinated nitrile by a free methanol.

Nitrile ligands in [*trans*-$C_6Cl_5Ni(L)_2(NCR)]^+$ have been converted to the corresponding imino—ether ligands [123]. With the exception

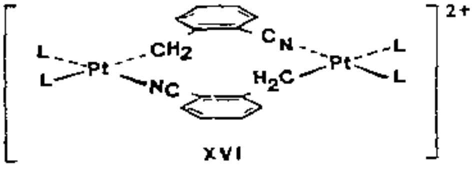
$[C_6Cl_5Ni(L)_2(NCR)]^+ + R_1OH \rightarrow [C_6Cl_5Ni(L)_2N(H) = C(OR_1)R]^+$

$L = PPhMe_2$; $RCN = CH_3CN, C_6H_5CH_2CN, C_6H_5CN$; $R_1OH = CH_3OH, C_2H_5OH$

$L = PPh_2Me$; $RCN = CH_3CN, C_6H_5CH_2CN$; $R_1OH = CH_3OH$

of the $C_6H_5CH_2CN$ reaction, a catalytic amount of triethylamine was required in order to obtain a reaction. The IR spectra of all the nitrile complexes used as starting materials displayed ν(CN) bands at higher frequencies than the free nitrile which is consistent with end-on coordinated nitrile groups.

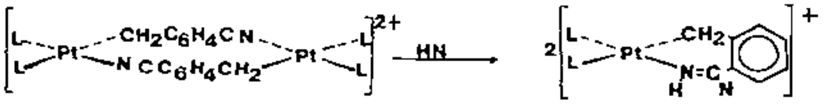
Ros et al. have synthesized a series of cationic platinum(II) complexes containing 2-$CH_2C_6H_4CN$ groups which are presumably of the following structure [124—126].



XVI

$L = PPh_3, \frac{1}{2}Ph_2PCHCHPPh_2$

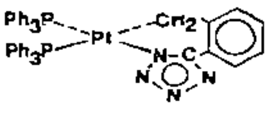
The nitrile groups in these complexes are very susceptible to nucleophilic attack and the triphenylphosphine containing complex readily reacts with alcohols, thiols, primary amines, and secondary amines to yield the corresponding imino-ether, imino-thioether, and amidine groups. The monomeric formulation for the products is favored on the basis of conductivity and



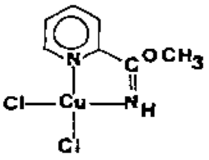
N = CH_3O, C_2H_5O, i-C_3H_7O, $C_6H_5CH_2O$, CH_3S,
C_2H_5S, $C_6H_5CH_2S$, $(CH_3)_2N$, $(C_2H_5)_2N$,
$(CH_3)(C_6H_5)N$, $C_5H_{10}N$, 4-$CH_3C_6H_4NH$,
4-$CH_3OC_6H_4NH$

spectroscopic data [125].

It has been proposed that the first step of the addition reaction is the coordination of HN in place of the nitrile and that this is followed by attack of the free nitrile group on the coordinated HN. The isolation of monomeric complexes of the type [*cis*-$L_2Pt(L')(CH_2C_6H_4CN)]^{+n}$ (L′ = N_3^-, NH_3) from the dimers has been accomplished [124] and is considered to be in accord with the proposal. Furthermore, the N_3^- complex yields a tetraazolate complex upon heating, presumably by attack of the free CN group on the coordinated N_3^- [124].

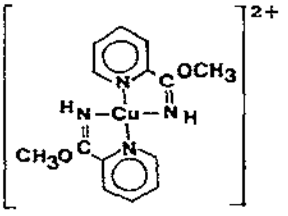


XVII

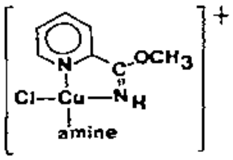


XVIII

Metal ions such as Cu^{2+} have been observed to promote the addition of alcohols to the nitrile group in cyanopyridines. Thus, an imino-ether complex, which has been assigned the structure shown in XVIII, has been obtained from a mixture of copper(II) chloride and 2-cyanopyridine in methanol [127]. Similarly, when amines (e.g., NH_3, CH_3NH_2, $(CH_3)_2NH$) were added to the mixture the following were obtained [128].

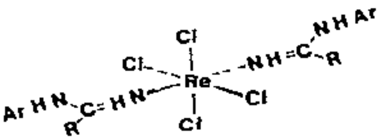


XIX



XX

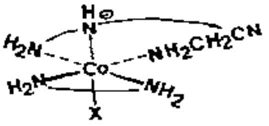
Amidine and imino-ether complexes have also been reported to result from the addition of primary aromatic amines, methanol, and ethanol to the nitrile groups in $Re(Cl)_4(NCR)_2$ (R = CH_3, C_6H_5) to yield, for example, XXI [129]. The platinum complex originally formulated as $Pt(NH_3)_4(CH_3CN)_2 \cdot Cl_2 \cdot H_2O$ has also been shown to be an amidine complex of the stoichiometry $[Pt(NH_3)_2[N(H)C(NH_2)CH_3]_2]^{2+}$ in which the imine nitrogens are bound to the platinum [130].



XXI

$R = CH_3$; $Ar = 4\text{-}C_6H_4CH_3$, $3\text{-}C_6H_4F$, $4\text{-}C_6H_4CO_2C_2H_5$,
$R = C_6H_5$; $Ar = 4\text{-}C_6H_4OCH_3$

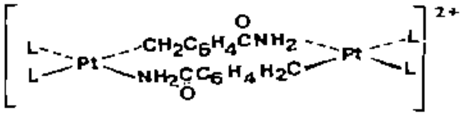
Attack on a nitrile carbon by a deprotonated —NH_2 group has been proposed to account for the tridentate amidine containing product $[Co(en)\text{-}[NH_2CH_2C(NH_2)NCH_2CH_2NH_2]Cl]^{2+}$ which results when $[cis\text{-}Co(en)_2(NH_2\text{-}CH_2CN)Cl]^{2+}$ is placed in neutral or basic solutions [131,132].



XXII

(ii) Reactions with water and hydroxide ion

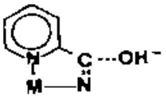
The majority of the studies of metal-catalyzed reactions of nitriles have focused on hydration reactions. For example, the platinum complex containing the bridging cyanoalkyl group, $[(PPh_3)_2PtCH_2C_6H_4CN]_2^{2+}$ (XVI), which was reported to react with alcohols, thiols and amines (vide supra) was also observed to hydrolyze yielding a dimeric amide containing complex XXIII [125]. Treatment of the amide with hydroxide ion was observed to yield the corresponding neutral imido complex. The imido complex was found to be dimeric by molecular weight measurements.



XXIII

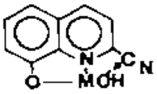
Bennett and Toshida have described the homogeneously-catalyzed hydration of nitriles by low-valent phosphine complexes [133]. Acetonitrile and propionitrile yielded 150 moles of acetamide and 300 moles of propionamide per mole of the catalyst *trans*-$Rh(OH)(CO)(PPh_3)_2$. Other catalysts studied include: $Pt(C_6H_8)(Dppe)$, $Pt(C_6H_8)(PPh_3)_2$, $Pt(CH_3)(NHCOCH_3)(PPh_3)_2$, $Pt(C_6H_9)(OH)(Dppe)$, *trans*-$Ir(OH)(CO)(PPh_3)_2$, and the aforementioned *trans*-$Rh(OH)(CO)(PPh_3)_2$. The authors conclude that M—OH species either present in the original catalyst or obtained from reaction with water are necessary before the complexes function as catalysts. Mechanistic details for these reactions have not been elucidated, but insertions into M—OH bonds are favored over intermediates involving side-on metal—nitrile interactions.

Several studies have been concerned with the metal-catalyzed hydration of the nitrile groups in 2-cyano-1,10-phenanthroline and 2-cyanopyridine which yield the corresponding carboxamides [127,134—138]. Breslow et al. have concluded that in these reactions the metal ions, such as Cu^{2+}, Ni^{2+}, and Zn^{2+}, serve to stabilize the negative charge which forms on the nitrogen when an external (uncoordinated) hydroxide ion attacks the nitrile carbon [134]. An analogous reaction scheme has been proposed to account for the isoxazoline product which results from the reaction of trishydroxymethylaminomethane with 2-cyanopyridine in the presence of Cu^{2+} [139].



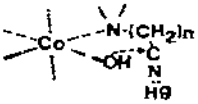
XXIV

The hydrolysis in basic solution of the cyano-group of 2-cyano-9-hydroxyquinoline has been studied recently [140]. As expected, the kinetic study results are in general agreement with those obtained by Breslow for 2-cyano-1,10-phenanthroline [134] and indicate that Ni^{2+}, Co^{2+} and Cu^{2+} strongly catalyze the hydration. It has been suggested that the mechanism may involve attack either by an uncoordinated hydroxide as shown in XXIV or by a coordinated hydroxide as shown in XXV.



XXV

Studies of the Hg^{2+}-catalyzed hydrations of the uncomplexed nitrile groups in *cis*-$[Co(en)_2(NH_2(CH_2)_nCN)X]^{2+}$ ($X = Br$; $n = 1, 2$) [141] ($X = Cl, Br$; $n = 1$) [132] have been reported. For these systems, the hydrolysis of the nitrile group was found to be strongly catalyzed by the Hg^{2+}. It was found that the rate of hydration of the propionitrile derivative ($n = 2$) was significantly slower than that of the acetonitrile derivative ($n = 1$). From the results obtained it was suggested that the reactions proceeded via a Hg^{2+} assisted removal of the coordinated X^- followed by attack on the nitrile carbon by a coordinated hydroxide group as shown below [141].



XXVI

Several studies have focused on the hydrolysis in basic solution of coordinated nitriles in complexes of the type $[M(NH_3)_5(NCR)]^{n+}$ ($M = Co, Ru, Rh, Ir$). Many of the studies have involved the Co(III) complexes $[Co(NH_3)_5(NCR)]^{3+}$.

$[(NH_3)_5Co(NCR)]^{3+} + OH^- \rightarrow (NH_3)_5CoN(H)C(O)R$

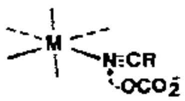
R	Me	Ph	3 and 4 PhOH	2, 3 and 4 PhCN	3 and 4 PhCHO	4 PhC(O)CH$_3$
Ref.	142	143	143	138, 144	138, 144	138, 144

Spectroscopic studies have been used to establish the end-on bonded nature of the nitrile in $[Co(NH_3)_5NCR]^{3+}$ and the N-bonded nature of the products [138,142—145]. For these Co(III) systems, the coordinated nitriles were found to hydrolyze about 10^6 times faster than the free nitriles. The data obtained are consistent with attack on the coordinated nitrile carbon by a free hydroxide ion.

Ford has recently expanded the base hydrolysis studies to include the d^5 and d^6 complexes $[Ru(NH_3)_5NCR]^{3+}$ ($R = CH_3, C_6H_5$) [146], $[Ru(NH_3)_5NCCH_3]^{2+}$ [146], $[Rh(NH_3)_5NCR]^{3+}$ ($R = CH_3, C_6H_5$) [146,147], and $[Ir(NH_3)_5NCC_6H_5]^{3+}$ [147]. The rates observed for the hydrolysis reactions of the Rh(III) and Ir(III) complexes were comparable to those observed for the Co(III) complexes. Within this series, the rates of hydrolysis of benzonitrile followed the order Co(III) > Rh(III) > Ir(III) with the difference between Co(III) and Rh(III) greater than that between Rh(III) and Ir(III). Ford has pointed out that this ordering follows that of the ionic radii, Co^{3+} (0.53 Å) < Rh^{3+} (0.67 Å) < Ir^{3+} (0.73 Å) and suggested that the rate differences for these metals are due mainly to the relative abilities of the metal centers to stabilize the negative charge which forms on the nitrile nitrogen [147].

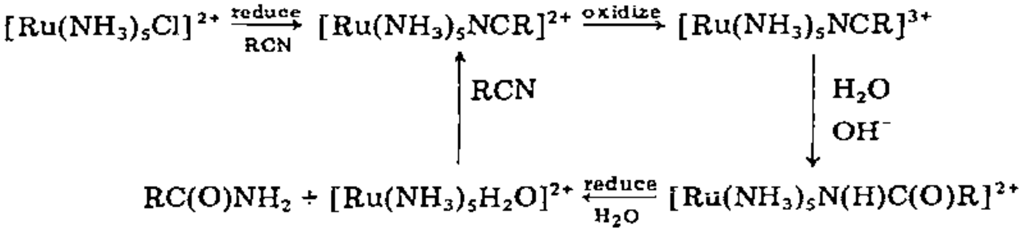
For the ruthenium complexes, marked differences between Ru(II) and Ru(III) were observed for the rates of hydrolysis [146]. The rate studies showed that Ru(III) provided a rate enhancement of about 10^8 which is the largest increase yet observed for a $[M(NH_3)_5NCR]^{+n}$ complex. In contrast, the rates observed for the Ru(II) complexes proved to be at least 10^6 slower than those of the Ru(III) complexes. The relative rates were rationalized in terms of the π-acceptor abilities of the metal centers, i.e. $Ru^{2+} \gg Ru^{3+}$ [146]. It was noted, however, that the rate of hydrolysis of benzonitrile was greater than that of acetonitrile for the $[Ru(NH_3)_5NCR]^{3+}$ complexes which is counter to the relative π-acceptor abilities of these nitriles. Thus, it was suggested that electronic effects in addition to the π-acceptor strengths are important in determining the rates.

Ford's study also showed that the buffers utilized in the hydrolysis reactions were involved in the reactions [146]. In accord with this observation, it was proposed that in the studies utilizing the CO_3^{2-}—HCO_3^- buffer, one pathway for the formation of the amido group could involve attack by the carbonate ion on the nitrile carbon.



XXVII

Ford has clearly established that marked differences exist between the nitrile complexes of Ru(II) and Ru(III) [33,146]. Taube has designed a catalytic system for the hydration of nitriles which is based on these differences [148,149]. The scheme, shown below,



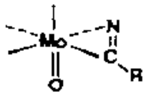
$$\begin{tikzcd}
{[Ru(NH_3)_5Cl]^{2+}} \arrow[r, "reduce", "RCN"'] & {[Ru(NH_3)_5NCR]^{2+}} \arrow[r, "oxidize"] & {[Ru(NH_3)_5NCR]^{3+}} \arrow[d, "H_2O \\ OH^-"] \\
& RC(O)NH_2 + {[Ru(NH_3)_5H_2O]^{2+}} \arrow[u, "RCN"] & {[Ru(NH_3)_5N(H)C(O)R]^{2+}} \arrow[l, "reduce"', "H_2O"]
\end{tikzcd}$$

is based on the ability of Ru(II) to stabilize nitrile coordination which encourages the nitrile to bond and the ability of Ru(III) to promote the hydrolysis.

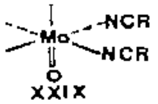
It has also been observed that $TiCl_4$ [150] and $PdCl_2$ [151] catalyze the hydration of nitriles. Chloro-, bromo-, and iodoacetonitrile were readily hydrolyzed by $PdCl_2$ and the corresponding amides obtained in yields of 70—80%. The $TiCl_4$ catalyst system which proved effective consisted of a mixture of $TiCl_4$, CH_3CO_2H, and H_2O. For the latter system, it was proposed that the hydrolysis proceeds through intermediates of the type $R-C\equiv N:TiCl_4$.

(iii) Reduction of the nitrile group

Schrauzer et al. have examined the mechanism of reduction of nitriles in systems modeled after nitrogenase [152,153]. The model systems, based on molybdate ion and sulfur containing ligands such as cysteine, catalyze the reduction of saturated nitriles to alkanes and NH_3, and the reduction of HCN to CH_3NH_2. The reductions are stimulated by the presence of ATP and inhibited by CO and N_2. A comparison of the results obtained from the reduction in the model system with the results obtained from nitrogenase indicates that molybdenum is the active site in both systems. The authors favored side-on, *dihapto*, Mo-nitrile interactions, XXVIII, over end-on interactions, XXIX.



XXVIII



XXIX

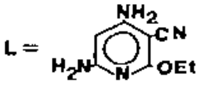
for the active sites in the non-enzymatic processes. For a related reaction see the reduction of $[Cp_2Mo(Cl)(CF_3CNH_2)]^+$ which is described in Sect. F(iv).

Fleisher and Krishnamurthy have reported that a mixture of the water soluble *meso*-tetra(*p*-sulfonatophenyl)porphyrinatocobalt(III) complex and sodium borohydride catalytically reduces acetonitrile [154]. The active reducing agent is proposed to be a Co(I) complex of the porphyrin.

Sargeson and Creaser have demonstrated that the end-on bonded nitrile ligands in $[Co(NH_3)_5NCR]^{3+}$ (NCR = NCMe, $NCCH_2CO_2Et$, $NC(CH_2)_2CH(COMe)_2$, $NC(CH_2)_4CN$, $NC(CH_2)_3NO_2$) are reduced by $NaBH_4$ at a rate that is at least 10^4 times as great as that of the free nitrile [155]. The reductions yield the corresponding amine complexes, and, for example, $[Co(NH_3)_5NH_2CH_2CH_3]^{3+}$ was obtained in 50% yield when the corresponding acetonitrile complex was treated with $NaBH_4$ in aqueous solution at a pH of 9.

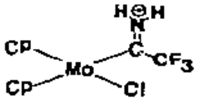
(iv) Miscellaneous reactions

It has been observed that the reaction of malononitrile, $NCCH_2CN$, with $ZnCl_2$ in ethanol yields a zinc complex of 2,4-diamino-5-cyano-6-ethoxypyridine (L) of the type $ZnCl_2L_2$ [156]. It was proposed that coordination of the malononitrile to the Zn promotes addition of ethanol to yield an iminoether, that the resulting NH group attacks the nitrile carbon of a second malononitrile, and that cyclization occurs to yield L.



XXX

Complexes of the stoichiometry Cp_2MoNCR have been obtained and it has been postulated that the nitrile groups are side-on coordinated (see Sect. C) [46]. The CF_3CN complex has been observed to react with gaseous HCl in toluene to yield a product which has been assigned the following iminium-containing formulation. This iminium-containing complex yields NH_3 and unidentified hydrocarbons when treated with $NaBH_4$.



XXXI

$$[Cp_2Mo(Cl)(CF_3CNH_2)]^+ + NaBH_4 \xrightarrow{OH^-} NH_3 + CpMoH_2 + \text{hydrocarbon}$$

Under the conditions reported, the reduction is not very efficient with only part of the iminium-containing complex undergoing reduction, and the yields of NH_3 are very low.

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