Chapter 10

Coordinated Isonitriles

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I. INTRODUCTION*

The versatility of the isonitriles is reflected not only by the variety of their reactions in organic chemistry, but by their ability to function as bonding partners for metals in complexes. In some respects, the chemistry of isonitrile metal complexes is simply inorganic coordination chemistry; by other criteria, the chemistry of coordinated isonitriles is organometallic or organic chemistry, although any formal distinction is purely artificial. A close examination of these isonitrile–metal complexes can often yield significant information on the mechanisms of organic isonitrile reactions.

Since the essential features of the ligands remain unchanged in the complexes, it is reasonable to consider the physical and chemical properties of the free isonitrile in an explanation of the chemistry of isonitrile ligands bonded to metals. In this connection, we consider the bonded isonitrile to be simply a free isonitrile which is perturbed by coordination. The structure and reactivity of complexed isonitriles vary not only with the isonitrile but also with the metal and its oxidation state in the complex. An attempt is made below to correlate these phenomena in terms of the metal and its oxidation state.

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* When this chapter was in the planning stage, very up-to-date review articles on metal–isonitrile chemistry were unavailable. At that time, it was the purpose of this chapter to catalog most or all of the references in this field and explain some of the important reactions. In the inevitable interim between conception and writing, the monograph *Isocyanide Complexes of Metals*[27] has appeared. Since this volume has successfully catalogued the references in this field, we have shifted the emphasis of this chapter to mechanism and explanation of some of the more important aspects of coordinated isonitrile chemistry.

II. STRUCTURE AND BONDING IN ISONITRILE COMPLEXES

When an isonitrile molecule coordinates to a metal, the lone electron pair of the formally divalent carbon atom forms a σ-type donor bond to the metal. If the metal has filled d-orbitals which are capable of overlapping with low-lying, empty antibonding orbitals of the attached ligand atom, a second bond of the π-type may be formed. In the case of isonitrile ligands, formation of this "back donating" bond can take place only with considerable rearrangement of the bonding system within the ligand since no such orbitals are available in the free ligand at the C atom. Back donation occurs to reduce the negative charge on the metal which is accumulated by the formation of the donor σ-bond. In isonitrile complexes of the same coordination number but of different charge, back donation increases as the positive charge on the complex decreases. This means that isonitriles, like some other ligands (CO, PF_3, etc.), are able to stabilize the low oxidation states of metals.

Some of these conclusions and interpretations are consistent with all of the experimental data; others are still ambiguous because different approaches seem to lead to different answers which will be discussed later.

IR spectroscopy is a most helpful tool for elucidating the structure and charge distribution of isonitriles as well as their complexes. The bond order of the isonitrile **CN** bond lies between 2 and 3. In an oversimplified but useful model the donor σ-bond provides a bond order that is essentially 3 (I) for the

$$\overset{\ominus}{M}\!\!\leftarrow\!\!C\!\!\equiv\!\!\overset{\oplus}{N}\!\!-\!\!R \qquad\qquad M\!\!\leftarrow\!\!\overset{\frown}{C}\!\!=\!\!\overset{-}{\overline{N}}\!\!-\!\!R$$

(I)   (II)

CN group which also prevails in the free ligand. A slight increase in the **CN** vibrational frequency seems to be due to a kinematic coupling of the **M—C** and **CN** bond.[10] Back donation and formation of a second **M—C** bond of the π-type is accompanied by a decrease of the **CN** stretching frequency corresponding to a contribution from structure II. While metals of the groups IB and IIB (Cu, Ag, Au, Zn, Cd, Hg) and rare earth metals[12] essentially form only σ-bonds with isonitriles, most of the other transition metals can also engage in π-bonding.
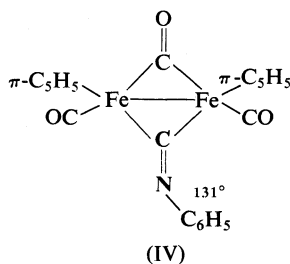
In a simple valence bond (VB) treatment,[10] structure II would require some deviation from linearity of the **CN—R** axis at the N atom as a result of the change in hybridization at the N atom, whereas molecular orbital (MO) considerations are consistent with a linear isonitrile molecule.[8]

In the case of trigonal bipyramidal $Co(CN—CH_3)_5^{+1}$ III[8] the **CNC** angle was found, by X-ray analysis, to be quite close to 180° (**CNC** < 177° ± 1.5 for axial ligands, **CNC** < 173° ± 2 for equatorial ligands).

R
|
N
|
R   C
| ⋮
N⋯
 ⋰   C ⋯
    ⋰   ⋰   ⋰
   C⋰ Co—C≡N—R
R—N⋯   C ⋯
      |
      C
      |
      N
      |
      R

(III)
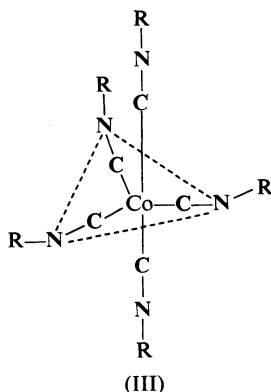
In a simple VB calculation this angle should decrease considerably, taking back donation into account, since the Co—C bond order was estimated to be 1.5 or greater. This estimate was made on the assumption that the Co—C bond was shortened compared to the sum of the covalent radii of cobalt and carbon.

Although this example is not in agreement with a simple VB calculation, there is at least one case known where a lowering of the CN bond order is accompanied by a bending of the CN—R axis. In complex IV[25] two iron atoms

O
‖
C
π-C$_5$H$_5$ π-C$_5$H$_5$
     \   ╱   ╲   ╱
OC—Fe———Fe—CO
     ╲   ╲   ╱
        C
        ‖
        N   131°
        \
        C$_6$H$_5$

(IV)

are bridged by phenyl isocyanide. Since the C atom already forms two bonds to the two iron atoms, the CN bond order should not exceed 2. This point is substantiated by the IR spectrum which shows the NC vibration at the very low frequency of 1704 cm^{-1} vs 2117 cm^{-1} for the free ligand. The X-ray analysis shows indeed that the isonitrile molecule is no longer linear but has a CNC angle of 131°. For a pure double bond we would expect approximately 120°, and for a pure triple bond, 180°. The IR data indicate a double, rather than a triple bond and the question becomes why is the CNC angle 11° greater than it should be, and not why is it 49° smaller than expected. The deriviation from linearity might be smaller than expected due to contact angles or crystal

forces; but one must also bear in mind that older X-ray data are subject to much greater uncertainty than that to which we are accustomed today,[8] and more precise data are needed before drawing any final conclusions.

The IR spectra of $Cr^0(CN-R)_6$ and $Ni^0(CN-R)_4$ could provide further criteria to test the validity of the VB and MO models. Since both complexes are highly symmetric (octahedral and tetrahedral configurations) they should exhibit only one NC stretching frequency unless back donation lowers the symmetry by bending the CNC axis. Back donation is also expected to reduce the negative charge on the zero valent metals. The fact that the IR spectra of both $Cr(CN-C_6H_5)_6$ (in $CHCl_3$, ν_{NC}: 2070, 2012, 1965 cm^{-1}) and $Ni(CN-C_6H_5)_4$ (in $CHCl_3$, ν_{NC}: 2050, 1990 cm^{-1}) show more than one CN—band, is taken as evidence that, in this case at least, the VB approach can afford an adequate explanation of the observations.[10] The IR spectra of Cr(O) and Ni(O) complexes are reported only for bulky isonitriles like phenyl isocyanide. In these complexes a deviation from the octahedral or tetrahedral symmetry might be caused simply by steric hindrance and subsequent deformation of the large ligand. Even for $Fe(CN-CH_3)_6^{2\oplus}$, where back donation is less likely to occur due to the positive charge on the central ion, two NC stretching frequencies have been reported (ν_{NC}: 2234 and 2197 cm^{-1}).[11]

One must use caution in evaluating the data obtained from IR measurements because these spectra are frequently obtained on solutions of the compounds in chlorinated solvents. These particular solvents are known occasionally to cause decomposition of the complex or to give rise to unexplained and spurious bands.[3,25] Further experimental data are needed for a consistent interpretation of the IR spectra of these complexes.

The geometry of coordinated isonitrile ligands can be qualitatively evaluated by considering the irreducible representations of those orbitals involved in bonding. If one views the complex along the axis formed by a CN bond, and this axis has a symmetry of C_n ($n \geqslant 3$) then the R—N—C bond angle should be ca. 180°, even if back donation occurs.[33] If the symmetry is lower than threefold, i.e., twofold, σ plane, etc., then some deviation from linearity can be expected. In this case the degeneracy of the two empty antibonding π-orbitals of the ligand which are responsible for back-donation splits, and this may cause the preference of a mirror plane symmetry for the ligand. The structures of the complexes $[Co(CN-CH_3)_5]ClO_4$ (III) and $(C_5H_5)_2Fe_2(CO_3)$ $(CN-C_6H_5)$ IV as resolved by X-ray analysis (see pages 218 and 219) support this explanation.*

The occurrence of back donation is not only influenced by the metal and its oxidation state. In addition, in the complex M—C≡N—R the residue R may also affect the charge distribution. In a complex like $(CH_3)_3SiNCMo(CO)_5$

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* The author gratefully acknowledges helpful discussions of the symmetry aspects of coordinated isonitriles with Professor Ernst Ruch.

the nitrogen is bound to a Si atom which has empty $d\pi$-orbitals. MO considerations show that back donation lowers the energy of the entire set of π-electrons which belong to the M—C—N—Si group.[9] As a consequence the difference in the CN stretching frequencies of $[(CH_3)_3SiNC]Fe(CO)_4$ and $(CH_3)_3Si$—NC is considerably bigger than the corresponding difference for $[t\text{-}C_4H_9$—NC]—$Fe(CO)_4$ and $t\text{-}C_4H_9$—NC.

For complexes with phenyl isocyanide as ligands the question arises as to how strong the interaction between the benzene ring and the M—CN moiety might be. The acceptor strength of C_6H_5—NC seems to be much greater than that of CH_3—NC as is indicated by a larger drop in the NC stretching frequency of phenyl isocyanide on complexation. This observation was interpreted as a contribution from formula VI[4,10]:

Electron withdrawing substituents in the *para* position of the benzene ring should favor formula VI and thereby decrease the NC stretching frequency, whereas electron-donating groups should have the opposite effect. The IR spectrum, however, does not indicate such an effect. Therefore, it can be concluded that interaction of the π-electrons of the benzene and the NC group is weak in the complex.[10]

On the other hand, NMR experiments indicate that there is at least some interaction between the d-electrons of the metal and the π-electrons of the benzene ring. In solutions of Co(II)— or Ni(II)— acetylacetonate and phenyl isocyanide, isocyanide–metal complex formation occurs.[24] Unpaired spin density of the paramagnetic metal ions is transferred to the benzene ring via the C and N atoms, resulting in changes in the chemical shifts of the ring protons. The direction and magnitude of those effects are only consistent with the occurrence of back donation by π-bonding with participation of the benzene ring.

No attempt was made to measure the NMR shifts and NC stretching frequencies for this same system; such studies would eventually lead to a correlation of the extent to which back donation and coupling with the benzene ring takes place.

In addition to the particular metal, its oxidation state and coordination number, and the residue R in the isonitrile R—NC, there is one further factor which influences the reorganization of the isonitrile bonding system when the free ligand coordinates. In a mixed complex $M(CN$—$R)_mL_n$ the extent to which back donation to the isonitrile takes place also depends on

the π-acceptor strength of the L ligands.[4,7,10,23,35] In the case of CO, for example, the π-acceptor strength of CO is so much greater than that of iso-nitriles, that the CO groups acquire almost all of the negative charge from the metal, leaving the CN—R group to form a σ-donor bond. This means that VIII (below) is preferred over VII.

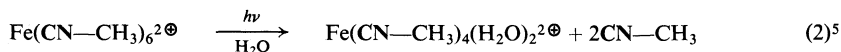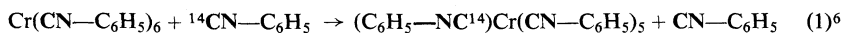$$\overset{\oplus}{|O}{\equiv}C \rightarrow \overset{2\ominus}{M} \leftarrow \overset{\oplus}{C}{\equiv}N{-}R \qquad \overset{-}{\underline{O}}{=}C{=}\overset{\ominus}{M} \leftarrow \overset{\oplus}{C}{\equiv}N{-}R$$

$$\text{(VII)} \qquad\qquad\qquad \text{(VIII)}$$

Substitution of one CO by phenyl isocyanide ($\nu_{NC} = 2117$ cm^{-1}) in Cr(CO)$_6$ slightly increases the NC stretching frequency for Cr(CO)$_5$CN—C$_6$H$_5$; ($\nu_{NC} = 2125$ cm^{-1}). The dipole moment of Fe(CO)$_4$CN—CH$_3$ (5.07 D)[22] is exceptionally large as compared to 3.5 D for the free isonitrile, and this is further evidence that in monosubstituted metal carbonyls the isonitrile does not participate in π-bonding. It also means that, considering the high sym-metry of the unsubstituted Fe(CO)$_5$ (trigonal bipyramid), the distance between the charges in $\overset{\ominus}{C}{\equiv}\overset{\oplus}{N}$—CH$_3$ increases on forming a σ-donor bond $M \leftarrow \overset{\ominus}{C}{\equiv}\overset{\oplus}{N}$—CH$_3$ whereas back donation

$$M \leftarrow \overset{-}{C}{=}N{-}R$$
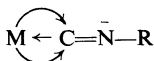
might even decrease the dipole moment. Substitution of more than one CO in metal carbonyls by isonitrile ligands also permits the isonitriles to participate in back donation.

III. REACTIONS OF COORDINATED ISONITRILES

As a consequence of the structural changes which occur when the isonitrile coordinates, the reactivity and chemical properties are different for the co-ordinated isonitrile than for the free ligand. In many cases the metal–isonitrile bond can be activated thermally or photochemically; this process generally leads to dissociation of one or more isonitrile ligands and substitution on the complex:

$$\text{Cr(CN—C}_6\text{H}_5)_6 + {}^{14}\text{CN—C}_6\text{H}_5 \rightarrow (\text{C}_6\text{H}_5\text{—NC}^{14})\text{Cr(CN—C}_6\text{H}_5)_5 + \text{CN—C}_6\text{H}_5 \quad (1)^6$$

$$\text{Fe(CN—CH}_3)_6{}^{2\oplus} \xrightarrow[\text{H}_2\text{O}]{h\nu} \text{Fe(CN—CH}_3)_4(\text{H}_2\text{O})_2{}^{2\oplus} + 2\text{CN—CH}_3 \quad (2)^5$$

It should be possible to form the metal complex of an isonitrile in order to protect the free ligand from reaction conditions which would otherwise destroy it.

By choosing a suitable complex one can change the charge distribution within the isonitrile to suit a particular reaction. Examples will be given to demonstrate this point.

Saegusa[34] (see Chapter 4) discovered that the α-addition of H—Y—R^1 compounds (Y = heteroatoms like O, N, P, Si, etc.) to isonitriles **CN—R^2** to yield R^1—Y—CH=N—R^2 are catalyzed by group IB and IIB metals (Cu, Ag, Zn, Cd, and Hg in various oxidation states). The first step in the reaction (3) is presumed to be coordination of the isonitrile to the metal by a σ-donor bond, as indicated by an increased stretching frequency in IX. Since negative charge is drained from the *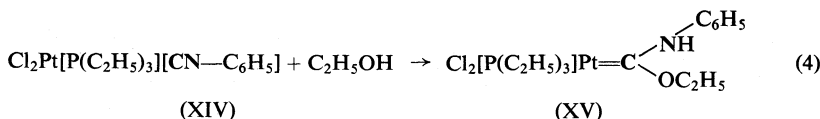*C** atom to the metal the carbon is now accessible to nucleophilic attack by a base, such as an alcohol R^{1}OH, which leads to the intermediate X. A subsequent proton transfer yields XI.

$$M + |\overset{\ominus}{C}\equiv\overset{\oplus}{N}-R^2 \;\rightarrow\; M-\overset{\ominus}{C}\equiv\overset{\oplus}{N}-R^2 \;\rightarrow$$

$$(IX)$$

$$(X) \qquad\qquad (XI) \qquad\qquad (XII) \qquad\qquad (XIII)$$

(3)
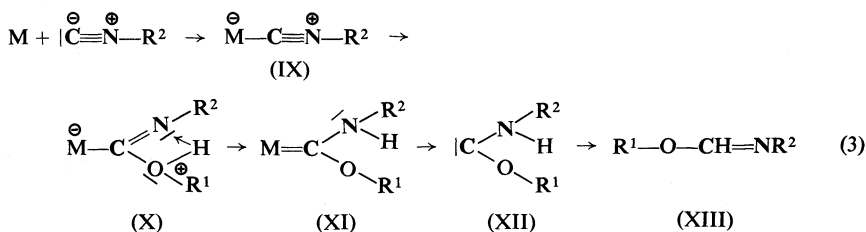
This, actually, is a carbene complex. For IB and IIB metals such complexes (XI) are quite unstable and tend to dissociate, leaving a high electron density at the carbon atom of XII. The free carbene finally stabilizes by proton transfer and forms XIII, the product of the catalysis.

The assumption of a carbene complex as an intermediate in this catalytic reaction (3) is supported by the fact that complexes with similar structures were recently synthesized by reactions like (4) of platinum isonitrile complexes with nucleophiles like alcohols and primary amines.[2]

$$Cl_2Pt[P(C_2H_5)_3][CN-C_6H_5] + C_2H_5OH \;\rightarrow\; Cl_2[P(C_2H_5)_3]Pt\!=\!C\!\!\underset{OC_2H_5}{\overset{NH-C_6H_5}{\big<}}$$

(4)

$$(XIV) \qquad\qquad\qquad\qquad\qquad (XV)$$

This structure for XV was confirmed by X-ray analysis. A small contribution from an ylide form XVa is indicated by a shortening of the **NC** bond to 1.32 Å. The existence of stable Pt carbene complexes may also explain why metals like platinum do not catalyze Saegusa's α-additions (see Chapter 4, Section I), because when the metal carbene complex is formed Pt binds the carbene ligand much more tightly than either Cu or Zn.

$$Cl_2[P(C_2H_5)_3]Pt-C\underset{OC_2H_5}{\overset{\overset{\oplus}{N}H-C_6H_5}{\diagup}}$$

(XVa)

$$Cl_2[P(C_2H_5)_3]PtCN-CH_3 + C_6H_5-NH_2 \rightarrow Cl_2[P(C_2H_5)_3]Pt{=}C\underset{NH-C_6H_5}{\overset{\overset{CH_3}{N}H}{\diagup}} \quad (5)$$

(XIVa)   (XVI)
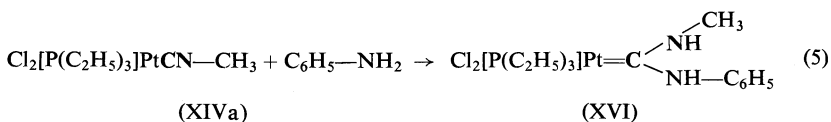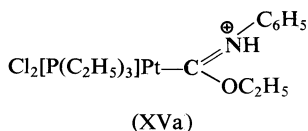
Strong bases like phenyllithium react with $Cr(CO)_6$ according to reaction (6). Methylation of the complex XVII leads to stable compound XVIII, the first carbene complex to be reported.[13]

$$(CO)_5\overset{\ominus}{Cr} \leftarrow C{\equiv}\overset{\oplus}{O}| + C_6H_5^{\ominus} \rightarrow$$

$$\left\{ (CO)_5\overset{\ominus}{Cr} \leftarrow C\underset{C_6H_5}{\overset{\overline{O}}{\diagup}} \longleftrightarrow (CO)_5\overset{\frown}{Cr} \leftarrow C\underset{C_6H_5}{\overset{\overset{\ominus}{O}|}{\diagup}} \right\} \rightarrow (CO)_5Cr{=}C\underset{C_6H_5}{\overset{OCH_3}{\diagup}} \quad (6)$$

(XVII)   (XVIII)
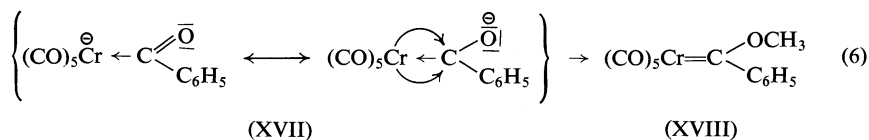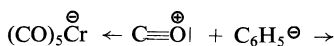
Reaction (7) is related to the formation of carbene complexes. The nucleophilic $C_6F_5^{\ominus}$ anion attacks the isonitrile carbon of XIX forming XX, which is a stable compound and can be considered an iminoacyl derivative of the iron complex.[36] The complex XX exists in two isomers; in which the methyl group
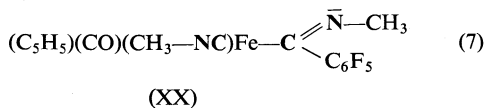
$$C_5H_5Fe(CO)(CN-CH_3)_2^{\oplus} + Li-C_6F_5 \rightarrow$$

$$(C_5H_5)(CO)(CH_3-NC)Fe-C\underset{C_6F_5}{\overset{\overline{N}-CH_3}{\diagup}} \quad (7)$$

(XIX)   (XX)

is either *trans* or *cis* with regard to the pentafluorophenyl group. The NC stretching frequency of XX (1580 cm^{-1}) is in accordance with the assumed structure; back donation from the metal to iminoacyl group is not likely to occur because it would put a negative charge on the nitrogen (XXa).

$$(C_5H_5)(CO)(CH_3-NC)\overset{\oplus}{Fe}{=}C\underset{C_6F_5}{\overset{\overset{\ominus}{N}-CH_3}{\diagup}}$$

(XXa)
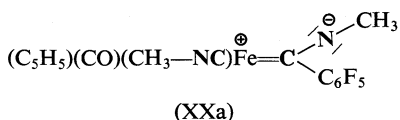
Protonation could perhaps yield the stable carbene complex cation XXb.

$$\left[(C_5H_5)(CO)(CH_3{-}NC)Fe{=}C{\overset{\overset{\displaystyle NH{-}CH_3}{\diagup}}{\underset{\underset{\displaystyle C_6F_5}{}}{\diagdown}}} \right]^{\oplus}$$

(XXb)
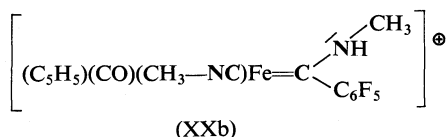
A similar mechanism was proposed to explain the insertion of cyclohexyl isocyanide into the nickel alkyl bond[40] of XXI [reaction (8)].

$$P(C_6H_5)_3(C_5H_5)Ni{-}R \xrightarrow[-P(C_6H_5)_3]{+2c\text{-}C_6H_{11}{-}NC} C_5H_5{-}Ni{\overset{\overset{\displaystyle CN{-}c\text{-}C_6H_{11}}{\diagup}}{\underset{\underset{\displaystyle \underset{\displaystyle c\text{-}C_6H_{11}}{|}}{\overset{\displaystyle N}{\|}}}{\diagdown C{-}R}}} \quad (8)$$

R = alkyl group

(XXI)   (XXII)

The alkyl anion is substituted by the isonitrile, and the subsequent nucleophilic addition of the alkyl group to the coordinated isonitrile yields the acyl imino complex XXII.

Reaction (9) was carried out to justify this mechanism.

$$[P(C_6H_5)_3(C_5H_5){-}Ni{-}(CN{-}c\text{-}C_6H_{11})]I \xrightarrow{C_6H_5MgBr}$$

(XXIII)

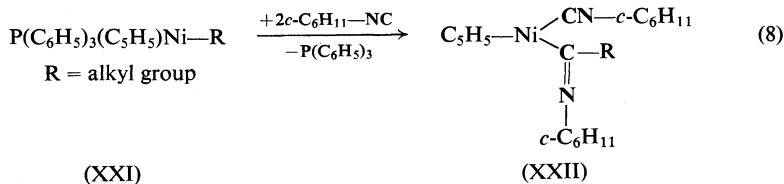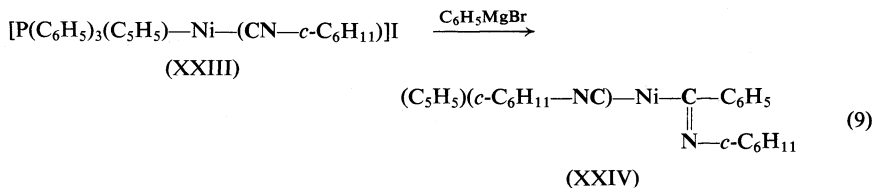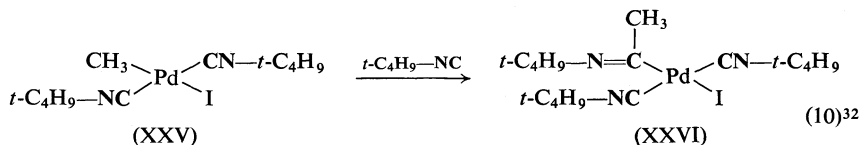$$(C_5H_5)(c\text{-}C_6H_{11}{-}NC){-}Ni{\overset{\overset{\displaystyle C{-}C_6H_5}{|}}{\underset{\underset{\displaystyle N{-}c\text{-}C_6H_{11}}{}}{\|}}} \quad (9)$$

(XXIV)

The palladium complex XXV reacts in analogy to the above iron and nickel complexes XIX–XXIII [reaction (10)]. Two alternative mechanisms are presented below. The methyl anion of XXV is mobile. As a strong nucleophile, it attacks one of the coordinated isonitriles. The resulting iminoacyl palladium complex is coordinately unsaturated, and this gap may be filled by a suitable donor, like an isonitrile, to stabilize the complex and yield XXVI.

$$\underset{t\text{-}C_4H_9{-}NC}{\overset{CH_3}{\diagdown}}Pd{\overset{\overset{\displaystyle CN{-}t\text{-}C_4H_9}{\diagup}}{\underset{\displaystyle I}{\diagdown}}} \xrightarrow{t\text{-}C_4H_9{-}NC} \underset{t\text{-}C_4H_9{-}NC}{\overset{t\text{-}C_4H_9{-}N{=}\overset{\overset{\displaystyle CH_3}{|}}{C}}{\diagdown}}Pd{\overset{\overset{\displaystyle CN{-}t\text{-}C_4H_9}{\diagup}}{\underset{\displaystyle I}{\diagdown}}}$$

(XXV)   (XXVI)   (10)[32]

The confirmed *trans* configuration of XXVI seems to favor the following alternative mechanism. The isonitrile ligand migrates first, and substitutes the methyl group which subsequently adds to the isonitrile.

The attempt to prepare the homologous nickel complex leads to surprising results. The reaction of XXVIII with methyl iodide in the presence of t-butyl isocyanide did not afford the expected product XXVII; a multiple successive insertion reaction of unknown mechanism leads to XXIX.

$$t\text{-}C_4H_9\text{—N}=\overset{\overset{\displaystyle CH_3}{|}}{C}\diagdown_{\underset{t\text{-}C_4H_9\text{—NC}}{}}\overset{}{\underset{}{Ni}}\diagup^{\diagup CN\text{—}t\text{-}C_4H_9}_{\diagdown I} \quad\xleftarrow{\;\;\not\;\;}\quad Ni(CN\text{—}t\text{-}C_4H_9)_4 \quad\longrightarrow$$

(XXVII)   (XXVIII)

$$(11)$$

(XXIX)

This structure is suggested by NMR and IR data ($\nu_{N\equiv C} = 2172\ cm^{-1}$; $\nu_{C=N} = 1667, 1634, 1610\ cm^{-1}$).

The complex XXIX seems to serve as an intermediate in the catalytic polymerization of isonitriles[39]; upon heating with an excess of isonitrile, XXX is formed.

$$\left[\begin{array}{c} R\text{—}N \\ \| \\ \text{—}C\text{—} \end{array}\right]_n$$

(XXX)

Another unusual insertion reaction occurs when an isonitrile reacts with the metal carbene complex.[1] The resulting complex XXXIII suggests that the isonitrile first substitutes the carbene ligand which (because of its high reactivity) adds to the NC multiple bond of the isonitrile ligand of XXXII.

$$(CO)_5Cr=C\diagup^{OCH_3}_{\diagdown CH_3} \;+\; c\text{-}C_6H_{11}\text{—NC} \;\rightarrow\; \left[\begin{array}{c} H_3C\diagdown_{\overset{\ominus}{C}}\diagup^{OCH_3} \\ (CO)_5Cr\text{—}C\overset{\oplus}{\equiv}N\text{—}c\text{-}C_6H_{11} \end{array} \right] \;\rightarrow$$

(XXXI)   (XXXII)

$$\left\{ \begin{array}{ccc} CH_3O\diagdown_C\diagup CH_3 & & CH_3O\diagdown_C\diagup CH_3 \\ | & \leftrightarrow & | \\ (CO)_5Cr\text{—}\underset{\ominus}{C}=\underset{\oplus}{N}\text{—}c\text{-}C_6H_{11} & & (CO)_5Cr=C\text{—}N\text{—}c\text{-}C_6H_{11} \end{array} \right\} \;\rightarrow\; (CO)_5Cr=C\diagup^{\overset{\displaystyle OCH_3}{|}C\diagdown^{OCH_3}_{CH_3}}_{\diagdown NH\diagdown_{c\text{-}C_6H_{11}}}$$

(XXXIII)   (XXXIV)

$$(12)$$

Nucleophiles like methanol attack the complex at the asymmetric carbon splitting the NC bond. As mentioned previously, a metal complex may serve as a protecting group for isonitriles. So it is even possible to stabilize isonitriles as ligands of complexes which do not exist in the free state. For example, the parent compound of all isonitriles "hydrogen isocyanide" XXXV cannot be isolated and exists only in equilibrium (13) with hydrogen cyanide XXXVa.

$$H\overset{\oplus}{-}N\overset{\ominus}{\equiv}C \; \rightleftharpoons \; H-C\equiv N \qquad (13)$$
$$(XXXV) \qquad (XXXVa)$$

But protonation of a complex XXXVI containing $CN^{\ominus}$ as a ligand can lead to a stable and well-characterized complex XXXVII with hydrogen isocyanide as a ligand[26]:

$$[(CO)_5Cr-NC]^{\ominus} + H^{\oplus} \; \rightarrow \; (CO)_5Cr-CN-H \qquad (14)$$
$$(XXXVI) \qquad\qquad (XXXVII)$$
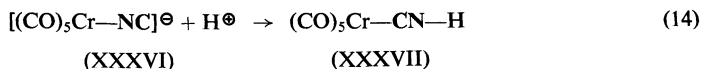
In analogy to this protonation, alkylation and arylation of metal cyanides is a more general way to prepare metal isonitrile complexes and finally free isonitriles.[21]

Olefins which tend to form carbonium ions by protonation alkylate cyanide ion in the presence of Cu(I)Br to form isonitriles.[30] The reactive intermediate is certainly a copper cyanide complex (see Chapter 2). When the copper salt is absent the reaction yields only nitriles.

Heldt has demonstrated another important application of metal complexes as protecting groups for isonitriles. Benzyl isocyanide is readily hydrolyzed by acids and hence cannot take part in electrophilic substitution reactions which have to be carried out in acidic medium. Since the complex XXXVIII is very resistant even to strong acids, it is possible to subject the coordinated

$$[(C_6H_5-CH_2-NC)_5FeCN]^{\oplus}$$
$$(XXXVIII)$$
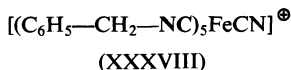
isonitrile to electrophilic substitution by HNO_3, SO_3, and CH_2O in concentrated sulfuric acid, and with bromine in acetic acid, leading to substitution at the aromatic ring.[19,21] Surprisingly, the substitution takes place almost exclusively at the *para* position of the benzene ring and only to a small extent at the *meta* position when more than one aromatic nucleus of the complex is being substituted. Since the NC stretching frequency of benzyl isocyanide ($\nu_{NC} = 2146$ cm^{-1}) increases to 2200 cm^{-1} in the complexed ligand, back donation appears not to take place and the complex XXXVIII is best represented

$$\overset{\ominus}{fe}-C\equiv\overset{\oplus}{N}-CH_2-C_6H_5 \quad \longleftrightarrow \quad fe=C=N-CH_2-C_6H_5$$
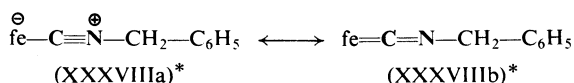
(XXXVIIIa)*   (XXXVIIIb)*

by formula XXXVIIIa. As Heldt pointed out, the positive charge at the nitrogen should be strongly *meta* directing in analogy to trimethylbenzylammonium chloride which on electrophilic substitution yields 88% of the *meta* isomer and only 12% of the *ortho* and *para* isomers. The anchimeric effect which was invoked to explain the reactivity of this complex is not very likely because it would require a fairly high contribution from formula XXXVIIIb.

According to the observations described above, the interaction of the NC group and the benzene ring, separated by a methylene group, does not seem to be very strong. The *para* position could just as well be favored to undergo substitution reactions because the *ortho* and *meta* positions are blocked by the steric bulk of the other ligands of XXXVIII. The fact that the mononitration of XXXVIII proceeds about 300 times faster than the nitration of benzene was taken as evidence for the enhanced reactivity of the coordinated isonitrile. Even so, one has to consider that the benzene is suspended only in sulfuric acid, and has to compete with the dissolved complex. The difference in the physical states of the competing aromatic rings might account for this observation. As described for the Saegusa reaction, nucleophiles attack the carbon atom of a coordinated isonitrile.

Heldt investigated the reactions of various nucleophiles with XXXIX,

$$[(C_6H_5-CH_2-NC)_5Fe-CN]Br$$

(XXXIX)
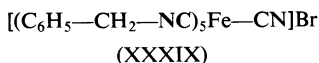
which take a different course, depending upon the nature of the nucleophile.[17] These experiments provide no evidence for back donation. As a consequence of the drain of electron density from the isonitrile carbon to the central metal of XXXIX, the complexed cyanide becomes a better leaving group, XL, by which the formation of a resonance stabilized benzyl cation is favored.
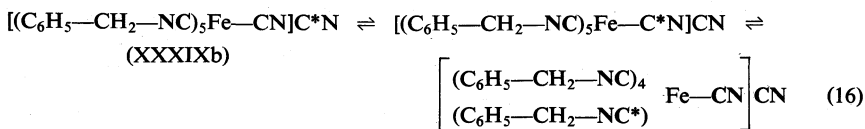
$$fe-C\equiv N-CH_2-C_6H_5 \;\rightleftharpoons\; [fe-C\equiv N|]^{\ominus} + \overset{\oplus}{C}H_2-C_6H_5 \qquad (15)$$

(XXXIXa)   (XL)   (XLI)
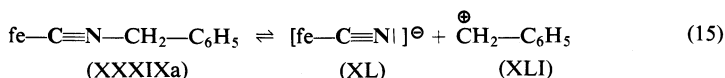
Most of the reactions of XXXIX with nucleophiles seem to be typical of the reactions of XLI.

Weak nucleophiles like $HOCH_3$, $HOCH(CH_3)_2$, HNH_2, $HNH(CH_2)_2CH_3$, and $HSCH_2CH_3$, which undergo α-additions in the Saegusa reaction, are alkylated by $[(C_6H_5-CH_2-NC)_5Fe-CN]Br$. Potassium thiocyanate yields benzyl thiocyanate which isomerizes to some extent to benzyl isothiocyanate.

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* We use lower case letters to represent a metal that is coordinately saturated, but where some of the ligands are not shown.

Bases like cyanide, which tend to coordinate strongly, react with the complex predominantly in a substitution reaction replacing the benzyl isocyanide, which hydrolyzes to N-benzylformamide under the reaction conditions.
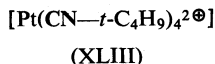
Tracer experiments [reaction (16)] with labeled $C^*N^\ominus$ demonstrate that the benzyl, cyanide, and isonitrile groups of XXXIXb scramble. This is further evidence for the intermediacy of the benzylcarbonium ion.

$$[(C_6H_5\text{---}CH_2\text{---}NC)_5Fe\text{---}CN]C^*N \;\rightleftharpoons\; [(C_6H_5\text{---}CH_2\text{---}NC)_5Fe\text{---}C^*N]CN \;\rightleftharpoons$$
(XXXIXb)

$$\begin{bmatrix} (C_6H_5\text{---}CH_2\text{---}NC)_4 \\ (C_6H_5\text{---}CH_2\text{---}NC^*) \end{bmatrix}Fe\text{---}CN \Bigg] CN \quad (16)$$
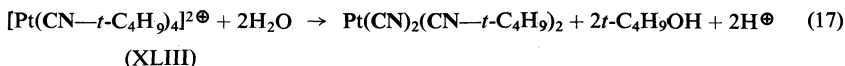
The formation of the benzyl cation can be utilized in a transalkylation reaction to synthesize new isonitrile complexes and subsequently new isonitriles.[18] If one adds to XXXIX an alkyl halide RX, which boils higher than the corresponding benzyl halide $C_6H_5\text{---}CH_2\text{---}X$, the benzyl halide can be removed from an equilibrium mixture by continuous distillation during formation of XLII.

$$[(R\text{---}NC)_5Fe\text{---}CN]^\oplus$$
(XLII)
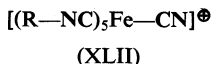
XLII can be hydrolyzed to yield the free isonitrile, R---NC. The tendency of XLIII to lose *t*-butyl carbonium ions is so great that the complex ion even

$$[Pt(CN\text{---}t\text{-}C_4H_9)_4{}^{2\oplus}]$$
(XLIII)

alkylates water to form *t*-butanol.[37]

$$[Pt(CN\text{---}t\text{-}C_4H_9)_4]^{2\oplus} + 2H_2O \;\rightarrow\; Pt(CN)_2(CN\text{---}t\text{-}C_4H_9)_2 + 2t\text{-}C_4H_9OH + 2H^\oplus \quad (17)$$
(XLIII)

Paraformaldehyde in concentrated sulfuric acid reacts with XXXIX to yield polymeric products.[20] The formaldehyde attacks the coordinated benzyl isocyanide at the *para* position of the aromatic ring to form the alcohol XLV which can be isolated as an intermediate.

(XXXIXa)   (XLV)
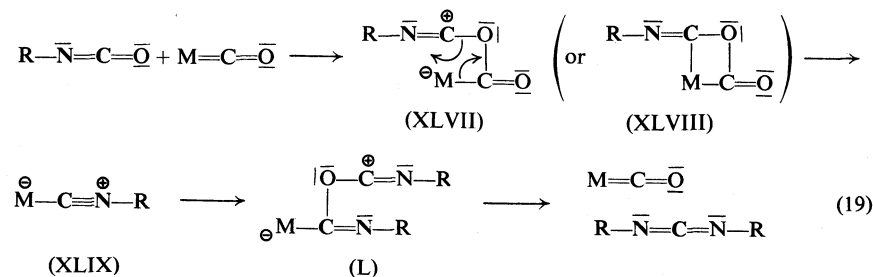

(XLVI)   (18)
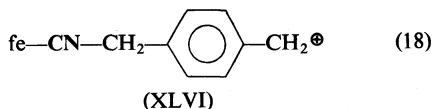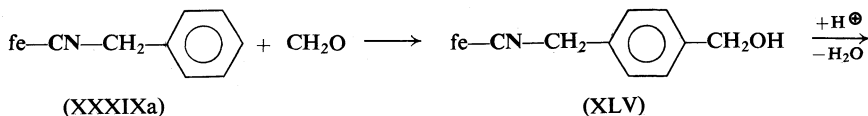
The next step is assumed to be the formation of a carbonium ion. An analysis of the polymer indicates that the carbonium ion XLVI may undergo three different reactions. It can react with benzyl isonitrile of the initial complex with formation of a methylene bridge which connects both aromatic rings at their *para* positions. It may attack the alcohol intermediate to yield an ether. Most surprising is the formation of an ethane bridge which requires the reduction of a carbonium ion to a radical and subsequent dimerization of two such radicals. The $Fe^{2\oplus}$ is oxidized to $Fe^{3\oplus}$, reducing the carbonium ion.

Since one ethane bridge was found per iron atom the complex ion has to undergo this internal redox process twice—but hardly simultaneously because it is impossible to form $Fe^{4\oplus}$ under the reaction conditions. It is feasible that after the first reduction takes place the $Fe^{3\oplus}$ is reduced to $Fe^{2\oplus}$, possibly by an excess of formaldehyde.

The conversion of isocyanates to carbodiimides and CO_2 is catalyzed by metal carbonyls [$Fe_2(CO)_9$, $Fe(CO)_5$, $W(CO)_6$, $Mo(CO)_6$]. This process represents a further illustration of the reactivity of isonitrile complexes which are intermediates in this reaction.[38]

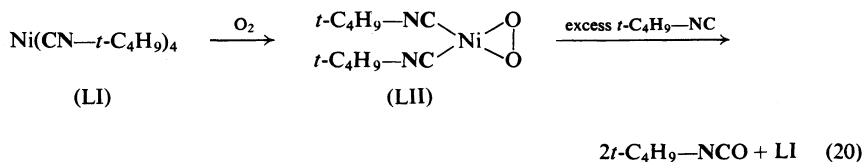The first step may be a nucleophilic attack of an isocyanate on a metal carbonyl (19).

$$R-\bar{N}=C=\bar{O} + M=C=\bar{O} \longrightarrow \underset{(XLVII)}{R-\overset{\oplus}{\bar{N}}=\overset{\ominus}{\underset{\oplus M-C=\bar{O}}{C-\bar{O}|}}} \left(or \ \underset{(XLVIII)}{\overset{R-\bar{N}=C-\bar{O}|}{\underset{M-C=\bar{O}}{|\quad|}}} \right) \longrightarrow$$

$$\underset{(XLIX)}{\overset{\ominus}{M}-C\equiv\overset{\oplus}{N}-R} \longrightarrow \underset{(L)}{\overset{|\bar{O}-\overset{\oplus}{C}=\bar{N}-R}{\underset{\ominus M-C=\bar{N}-R}{|}}} \longrightarrow \underset{R-\bar{N}=C=\bar{N}-R}{M=C=\bar{O}} \qquad (19)$$

It is questionable whether the cyclic intermediate XLVIII is involved as Ulrich has suggested, because in the cases of $Mo(CO)_6$ or $W(CO)_6$ the formation of an unusual, heptacoordinated monosubstituted metal carbonyl is required. Also the simultaneous bond making and bond breaking of XLVII to form the isonitrile complex XLIX and release of CO_2 seems to be quite plausible.

A second isocyanate now attacks the isonitrile carbon of XLIX to form L which is finally stabilized, releasing the metal carbonyl and the carbodiimide.

When the metal carbonyl is employed in excess, the reaction yields metal carbonyls in which some of the carbonyl groups are substituted by isonitrile[28,38] which confirms the formation of an isonitrile complex as an intermediate in the catalytic conversion of isocyanate to carbodiimide.

In the absence of catalysis molecular oxygen does not oxidize isonitriles to isocyanates. This reaction is catalyzed by certain transition metals in low oxidation states (Ni^0, Co^0, $Rh^\oplus$).[31] The isolation of a Ni isonitrile peroxo complex LII which is formed by reaction (20) suggests the formation of LII

$$Ni(CN\!\!-\!\!t\text{-}C_4H_9)_4 \xrightarrow{\ O_2\ } \begin{matrix} t\text{-}C_4H_9\!\!-\!\!NC \\ t\text{-}C_4H_9\!\!-\!\!NC \end{matrix}\!\!>\!\!Ni\!\!<\!\!\begin{matrix} O \\ | \\ O \end{matrix} \xrightarrow{\ \text{excess }t\text{-}C_4H_9\!\!-\!\!NC\ }$$

$$\quad\text{(LI)} \qquad\qquad\qquad\qquad \text{(LII)}$$

$$2t\text{-}C_4H_9\!\!-\!\!NCO + LI \quad (20)$$

as an intermediate in the catalytic oxidation of isonitriles.

IV. THE SYNTHESIS OF METAL ISONITRILE COMPLEXES

The synthesis of isonitrile metal complexes is described in great detail by Malatesta and Bonati.[27] Therefore, only a brief general outline of the methods is given here.

There are three general ways to prepare isonitrile complexes.

1. The synthesis of an isonitrile complex by alkylation of silver ferrocyanide by Freund (21)[14] (see also Chapter 2) is representative for a general way to

$$Ag_4Fe(CN)_6 + 4C_2H_5\!\!-\!\!I \ \rightarrow \ (C_2H_5\!\!-\!\!NC)_4Fe(CN)_2 + 4AgI \quad (21)$$
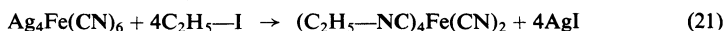
obtain isonitrile complexes and furthermore free isonitriles, since the coordinated ligands can be released by substitution reactions.

The mechanism of the alkylation is not known. It may involve the formation of a carbonium ion ($C_2H_5^\oplus$) which reacts with the cyanide complex.

The reaction is very slow and often does not give well-defined products, possibly indicating an equilibrium reaction.[21]

Another alkylating agent is dimethylsulfate.[15] $H_4Fe(CN)_6$ reacts with diazomethane[29] and even with alcohol[16] to give isonitrile complexes.

The transalkylation reaction mentioned above extends the limited application of the simple alkylation reaction.

2. A general and very useful procedure for the preparation of isonitrile complexes simply requires mixing of a metal salt and the isonitrile.

$$MX_n + {}_mR\!\!-\!\!NC \ \rightarrow \ [M(CN\!\!-\!\!R)_m]X_n \quad (22)$$

Sometimes the reaction is carried out in a solvent when mild conditions are required in order to avoid polymerization. Often an excess of isonitrile reduces

the metal to a lower oxidation state which is stable in the isonitrile complex.
3. Substitution of the ligand L in the complex by isonitriles also leads to

$$ML_x + yR{-}NC \longrightarrow ML_{x-y}(CN{-}R)_y + yL \tag{23}$$
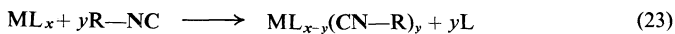
isonitrile complexes. The application of this method is limited by the fact that frequently—especially in the case of metal carbonyls—not all ligands L are replaced by isonitrile. The reaction of isocyanate with metal carbonyls can be considered to be a special case of this method.[28,38] The mechanism of this reaction has already been discussed.

REFERENCES

1. Aumann, R., and Fischer, E. O., *Chem. Ber.* **101**, 954 (1968).
2. Badley, E. M., Chatt, J., Richards, R. L., and Sim, G. A., *Chem. Commun.* p. 1322 (1969).
3. Bamford, C. H., Eastmond, G. C., and Hargreaves, K., *Nature* **205**, 385 (1965).
4. Bigorgne, M., and Bouquet, A., *J. Organometal. Chem.* **1**, 101 (1963).
5. Carassiti, V., Condorelli, G., and Condorelli-Costanzo, L. L., *Ann. Chim. (Rome)* **55**, 329 (1965).
6. Cetini, G., and Gambino, O., *Ann. Chim. (Rome)* **53**, 236 (1961).
7. Cotton, F. A., *Inorg. Chem.* **3**, 703 (1964).
8. Cotton, F. A., Dunne, T. G., and Wood, J. S., *Inorg. Chem.* **4**, 318 (1965).
9. Cotton, F. A., and Parish, R. V., *J. Chem. Soc.* p. 1440 (1960).
10. Cotton, F. A., and Zingales, F., *J. Amer. Chem. Soc.* **83**, 351 (1961).
11. Fabbri, G., and Cappellina, F., *Ann. Chim. (Rome)* **48**, 909 (1958).
12. Fischer, E. O., and Fischer, H., *J. Organometal Chem.* **6**, 141 (1966).
13. Fischer, E. O., and Maasböl, A., *Angew. Chem.* **76**, 645 (1964).
14. Freund, M., *Chem. Ber.* **21**, 931 (1888).
15. Hartley, E. G. J., *J. Chem. Soc.* **97**, 1066 (1910).
16. Heldt, W. Z., *J. Org. Chem.* **26**, 3226 (1961).
17. Heldt, W. Z., *J. Inorg. Nucl. Chem.* **24**, 73 (1962).
18. Heldt, W. Z., *J. Inorg. Nucl. Chem.* **24**, 265 (1962).
19. Heldt, W. Z., *J. Org. Chem.* **27**, 2604 (1962).
20. Heldt, W. Z., *J. Org. Chem.* **27**, 2608 (1962).
21. Heldt, W. Z., *Advan. Chem. Ser.* **37**, 99 (1963).
22. Hieber, W., and Weiss, E., *Z. Anorg. Allg. Chem.* **287**, 223 (1956).
23. Horrocks, W. D., and Taylor, R. C., *Inorg. Chem.* **2**, 723 (1961).
24. Horrocks, W. D., Taylor, R. C., and LaMar, G. N., *J. Amer. Chem. Soc.* **86**, 3031 (1964).
25. Joshi, K. K., Mills, O. S., Pauson, P. L., Shaw, B. W., and Stubbs, W. H., *Chem. Commun.* p. 181 (1965).
26. King, R. B., *Inorg. Chem.* **6**, 25 (1967).
27. Malatesta, L., and Bonati, F., "Isocyanide Complexes of Metals." Wiley, New York, 1969.
28. Manuel, T. A., *Inorg. Chem.* **3**, 1703 (1964).
29. Meyer, J., Domann, H., and Mueller, W., *Z. Anorg. Allg. Chem.* **230**, 336 (1937).
30. Otsuka, S., Mori, K., and Yamagami, K., *J. Org. Chem.* **31**, 4170 (1966).
31. Otsuka, S., Nakamura, A., and Tatsuno, Y., *Chem. Commun.* p. 836 (1967).
32. Otsuka, S., Nakamura, A., and Yoshida, T., *J. Amer. Chem. Soc.* **91**, 7196 (1969).

33. Ruch, E., private communication (1969).
34. Saegusa, T., Ito, Y., Kobayashi, S., Hirota, K., and Yoshika, H., *Tetrahedron Lett.* p. 6121 (1966).
35. Strohmeier, W., and Hellmann, H., *Chem. Ber.* **97**, 1877 (1964).
36. Treichel, P. M., and Stenson, J. P., *Inorg. Chem.* **8**, 2563 (1969).
37. Tschugaeff, L., and Teearu, P., *Chem. Ber.* **47**, 2643 (1914).
38. Ulrich, H., Tucker, B., and Sayigh, A. A. R., *Tetrahedron Lett.* **18**, 1731 (1967).
39. Yamamoto, Y., and Hagihara, N., *Bull. Chem. Soc. Jap.* **39**, 1084 (1966).
40. Yamamoto, Y., Yamazaki, H., and Hagihara, N., *J. Organometal. Chem.* **18**, 189 (1969).