

Emergence of a CNH and Cyano Complex Based Organometallic Chemistry[†]

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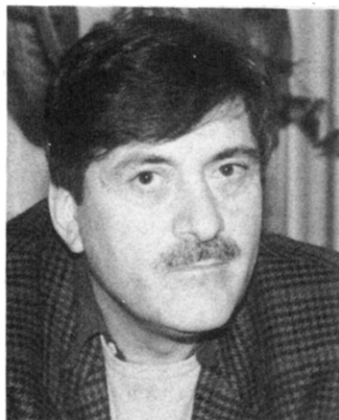
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I. Introduction

Cyano complexes are probably the longest-known coordination compounds whose chemistry may be said to have started with the discovery of Prussian Blue in 1704 by Diesbach, a Berlin painter. Their ubiquity in classical inorganic chemistry explains itself by the outstanding ligand properties of cyanide which forms complexes with virtually all metals often in various oxidation states. At intervals, the developments of the field or of special subsections thereof have been covered by several valuable in-depth reviews, Sharpe's book being by far the most comprehensive and useful.¹⁻¹⁰ In spite of all that, surprisingly, no chemistry of the coordinated cyanide ligand, apart from the well-known N-alkylation, has been developed which may in fact have to do with the "overwhelming ability of cyanide to complex" (thus displacing the other ligands),¹¹ although certainly more with its supposed inactivity and the insolubility of the complexes in organic media caused by the ionic nature and the high charges brought in by the $\{CN^-, cat^+\}$ ligands. Actually, save for some cyanations and large-scale hydrocyanations,¹² cyanide merely acts as a spectator or "dummy" ligand, e.g. in the so-called higher order organocuprates^{13,14} or in certain carbonylation $[[Ni(CN)(CO)_3]^-]$, $[Ni(CN)_2(CO)_2]^{2-}$ ^{15,16} and hydrogenation catalysts (e.g. $[Co(CN)_5]^{3-}$),^{17,18} or is completely absent from organo-transition metal reactions. Its difference from the isolobal or even isoelectronic carbon monoxide which plays the dominating role as a center of reactivity all over organometallic chemistry could thus not be greater and has routinely been attributed to the relative weakness of CN^- as a π -acid.¹⁹

Recently, however, reactions at the coordinated cyanide other than N-alkylation or CN transfer onto organic substrates have been found and further investigated in Beck's group in Munich as well as in our laboratories in Erlangen and in Berlin, thereby "strengthening the link with organometallic chemis-

[†] Dedicated to Professor Dr. Dr. mult. Heinrich Nöth on the occasion of his 65th birthday.



Wolf Peter Fehlhammer was born in München on September 9, 1939. He received his Dr. rer. nat. degree (with Professor Wolfgang Beck) from the Technische Hochschule München in 1968. After a DAAD postdoctoral position with Larry Dahl at the University of Wisconsin he returned to the University of München where he worked for his "Habilitation". In 1976 he joined the faculty at the Friedrich-Alexander-Universität of Erlangen-Nürnberg in Erlangen; there he was appointed Professor of Inorganic Chemistry in 1978. Since 1983 he has been a full professor at the Free University of Berlin. His principal research interests are in the fields of organometallic and coordination chemistry.



Marcus Fritz was born in Ulm (Baden-Württemberg) in 1963. He studied chemistry at the Universität of Ulm (1983–1989) finishing with a diploma thesis on "trace element analysis in ultra-pure quartz". After the military service he began his Ph.D. research work under the supervision of Professor W. P. Fehlhammer, dealing with cyano complexes as ligands for d metals. From 1990 to 1992 he has been recipient of a scholarship of the Graduiertenkolleg at the FU and TU, Berlin.

try".¹⁰ These new reactions comprise "radical alkylations" of cyano ligands, hydroisocyanations with CNH complexes, diverse cycloadditions to the CN ligand, and CN cleavage processes, all with retention of the metal-carbon bond; they are dealt with in sections III.B–E, while III.A is a résumé of earlier and recent electrophilic additions to cyano complexes giving rise, among others, to novel *functional* isocyanides.

This is preceded by a survey of the basic materials used in these investigations or, at least, projected for future use. Note that in the chapter on CNH complexes (section II.A) simple *reactions*—the formation of H-bonded adducts—are also discussed which are thought to represent the introductory step for most CNH transformations. Section II.B contains a very arbitrary and by no means comprehensive collection of cyano complexes of different character—"organometallic", "bioinorganic", etc.—again with promising applications in the organometallic chemistry of cyano complexes

just emerging. For unknown reasons, cyano complexes having typical organic coligands (η -C₅H₅, η -arene) had largely been excluded from most previous reviews, the only bonanza for "organometallic" cyano species being Turco and Riga's article on cyano phosphine complexes.⁸ The question of isocyano complexes, CN \rightleftharpoons NC isomerizations, and CN-bridged systems^{3,7}—all of relevance for a thorough exploitation of the synthetic potential of cyanide—will be slightly touched (sections II.C and D) with the intention to provide the desirable background and to familiarize the reader with related modern trends and current interests (also of the authors) in cyanometal complexes in toto which presently seem to experience a truly general renaissance.

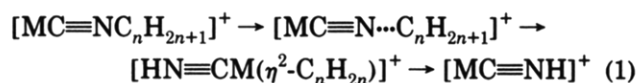
II. Basic Materials

A. Metal Complexes Containing the CNH Ligand

1. Gas-Phase and Surface Species

Although hydrogen isocyanide (HNC) is less stable than HCN by some 10–20 kcal mol⁻¹,²⁰ both species are known to coexist in comparable amounts in interstellar space (and probably even outside the Galaxy²¹), i.e. under collision-free conditions precluding any *intermolecular* isomerization processes.²² Also, the alternative of an *intramolecular* route is blocked due to a high barrier (40–50 kcal mol⁻¹) for the required [1,2]-hydrogen shift.^{20,23} Interestingly, the order of stability is reversed in the ionized forms of HCN/HNC, HCN⁺ and HNC⁺, whereas the barrier for the respective [1,2]-hydrogen migration (44.4 kcal mol⁻¹) is not substantially affected.^{23,24}

The most simple metal complexes of HNC, too, are encountered in the gas phase using mass spectrometry methodologies. Thus, "very stable" [MCNH]⁺ ions with "end-on" structures are observed for most of the d-block transition metals in collision activation mass spectra of complexes of the bare metal ions with short chain alkyl isocyanides. The highest abundance is found for group 6 and 11 metals, i.e. ions with half (d⁵) or completely filled (d¹⁰) shells. Isocyanide degradation mainly proceeds via an ion/dipole mechanism with preferential loss of the weaker bound alkene (eq 1).²⁵ Fragmentation



by electron impact of "real" isocyanide complexes follows a similar pattern.²⁶ Recently, gas-phase organometallic chemistry succeeded in the generation and identification of the "stable" *neutral* complex Cu⁰CNH with a lifetime > 0.8 μ s.²⁷

In striking contrast, the reaction of a clean Pt(111) surface with dilute aqueous solutions of metal cyanides gave rise to a highly ordered layer of isolated CN⁻ anions surrounded by platinum-bonded "upright" neutral hydrogen isocyanide molecules (Figure 1).²⁸

2. Discrete CNH Complexes in Condensed Phases

The most straightforward laboratory procedure for the synthesis of hydrogen isocyanide complexes is

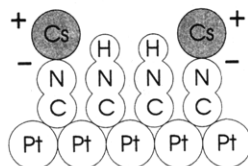


Figure 1. Surface structure of Pt(111)CsCN at $4 \leq \text{pH} < 9.28$

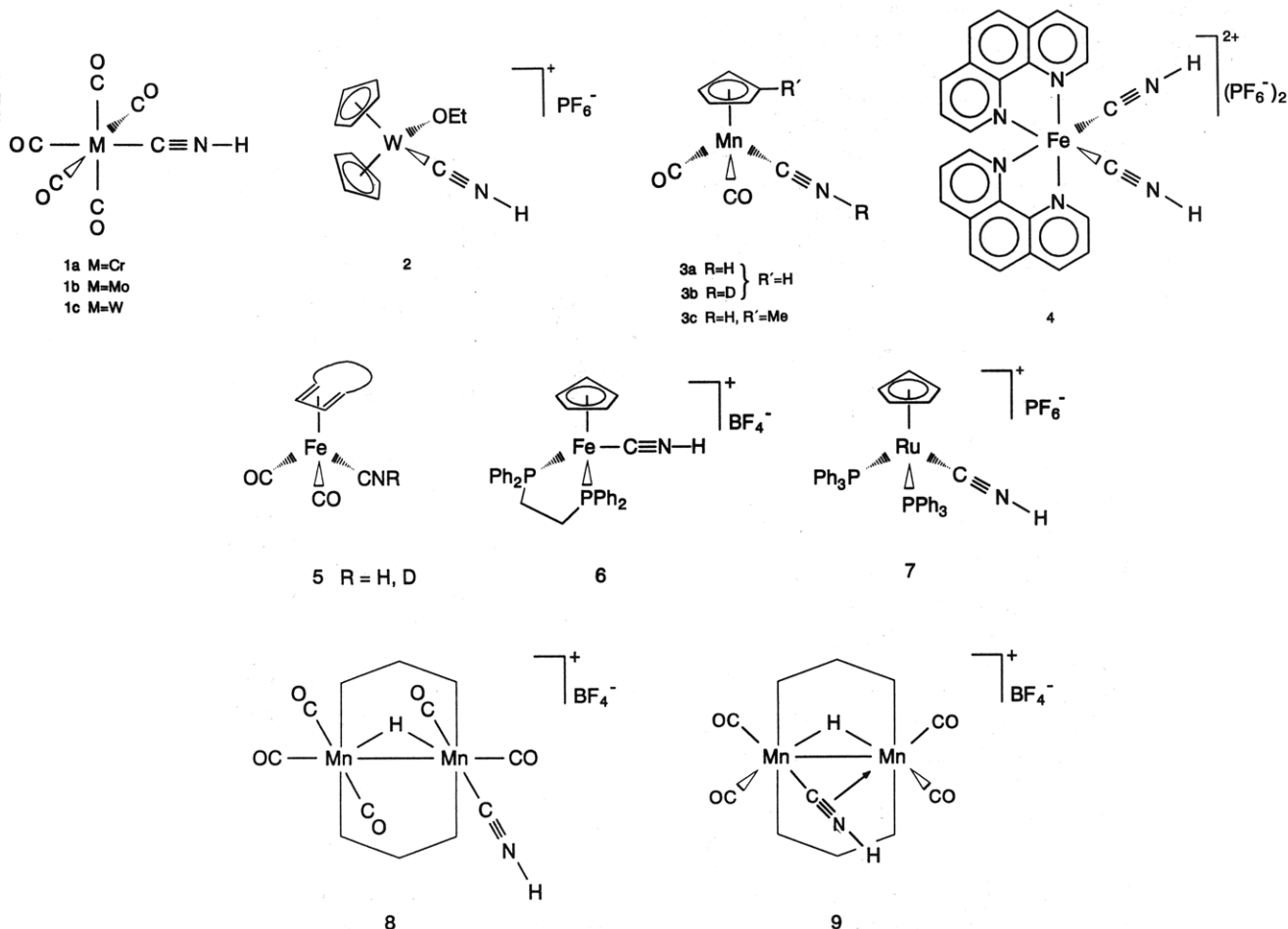
N-protonation of metal-coordinated cyanide. In fact, $[\text{M}]\text{CNH}$ species appear to be ubiquitous, particularly in acidic media, and many an acid-catalyzed aquation reaction of cyano complexes is believed to proceed via short-lived intermediates of that type.²⁹ More interestingly from the standpoint of organic synthesis, protonation of one of the cyano ligands in organo(pentacyano)cobaltates promotes the migration of the organic group R probably to the carbon atom of the CNH ligand with formation of the "insertion" product $[\text{Co}(\text{CN})_4\{\text{C}(\equiv\text{NH})\text{R}\}\text{aq}]^{2-}$.³⁰ Other hydrogen isocyanide complexes have clearly been identified in acidic solutions,^{31,32} yet only in rare instances has this route led to the isolation of discrete hydrogen isocyanide-metal compounds such as 1–8 which serve as the main basis for the investigation of a CNH chemistry.^{33–42}

However, there are also more incidental routes to CNH complexes such as aging of solid $[\text{Ru}(\text{NH}_3)_5\text{NCH}](\text{PF}_6)_2$ (!).⁴³ This slow intramolecular rearrangement of an N-bound hydrogen cyanide to a C-bound hydrogen isocyanide resulting in labilization of the trans ammonia and subsequent polymerization (to give CN-bridged polynuclear species) is reminiscent of the remarkable

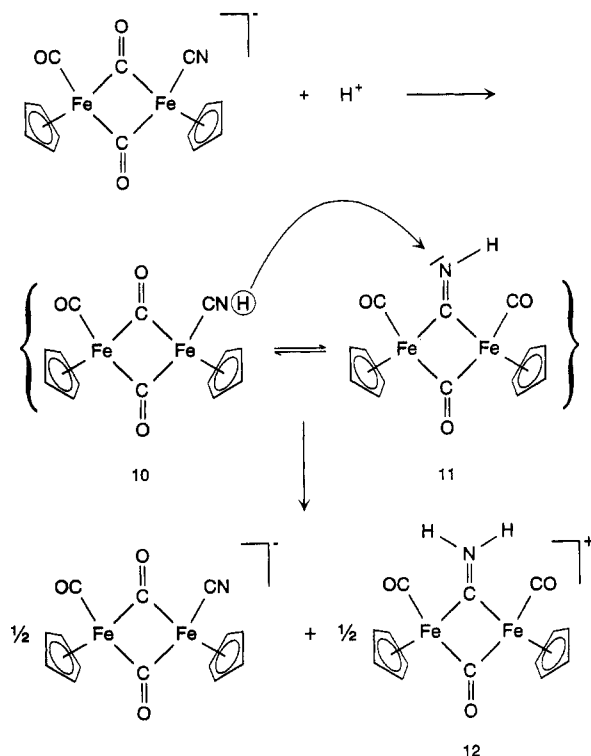
isomerization of N-bound imidazole to the C-bound form, again at ruthenium(II),⁴⁴ and has its parallel, e.g., in the slow to rapid isomerizations of NCSiMe_3 to CNSiMe_3 at manganese(I) and chromium(0) centers.^{45,46} Also note the various more or less unintended formations e.g. of $\text{trans-}[\text{Mn}(\text{CO})_2(\text{CNH})\{\text{P}(\text{OPh})_3\}\text{dppm}]^{2+/1+}$ from chemical oxidation with NO^+ of the corresponding cyanomanganese(I) complex,⁴⁷ and of $\text{Cr}(\text{CO})_5\text{CNH}$ by "radical alkylation" of $[\text{Cr}(\text{CN})(\text{CO})_5]^-$ in benzene (cf. section III.B),⁴⁸ or by solvolysis with ROH of $\text{Cr}(\text{CO})_5\text{CNCOMe}$ ⁴⁹ and $\text{Cr}(\text{CO})_5\text{CNSiMe}_3$.⁵⁰

Unfortunately, none of these neutral and cationic complexes (1–8, Chart I) has to date been characterized by X ray or neutron diffraction (see, however, below) so that the above structures are based solely on chemical plausibility and fragmentary IR data. Plausible IR assignments have been made of the $\nu(\text{NH})$ and $\nu(\text{NC})$ bands of 2 and 4–7 and, on the basis of isotopic shifts of deuterated samples, of 3a,b³⁶ in which the $\nu(\text{NC})$ bands [3a (KBr) 2016 vs; 3b 1968 vs cm^{-1}] has experienced a remarkable downward shift as compared to the parent cyano complex $[\text{Na}[\text{Mn}(\text{CN})\text{Cp}(\text{CO})_2](\text{KBr}) 2058 \text{ vs } \text{cm}^{-1}]$. A similar drop in the $\nu(\text{NC})$ frequency on protonation has been observed for 3c, 6, and 7 $[\text{Ru}(\text{CN})\text{Cp}(\text{PPh}_3)_2 (\text{nujol mull}) 2070 \text{ s; } 7 2024 \text{ w } \text{cm}^{-1}]$ while in 2, 4, and 8 the $\nu(\text{NC})$ bands have rather shifted slightly, respectively, to much higher wavenumbers $[\text{W}(\text{CN})\text{Cp}_2(\text{OEt}) (\text{KBr}) 2105 \text{ s; } 2 2133 \text{ s } \text{cm}^{-1}; \text{Mn}_2\text{H}(\text{CN})(\text{CO})_5(\text{dppm})_2 (\text{CH}_2\text{Cl}_2) 2091 \text{ w; } 8 2143 \text{ cm}^{-1}]$. The uncertainty existent in the case of $[\text{M}(\text{CN})(\text{CO})_5]^-$ as to which band in the 2150–1800- cm^{-1}

Chart I^a



^a 1a–c, refs 33 and 34; 2, ref 35; 3a–b, ref 36; 3c, ref 37; 4, ref 38; 5, ref 39; 6, ref 40; 7, ref 41; 8, ref 42; 9, ref 42.

Scheme I. Acid-Base Disproportionation of $\text{Fe}_2\text{Cp}_2(\text{CO})_3\text{CNH}^{55}$


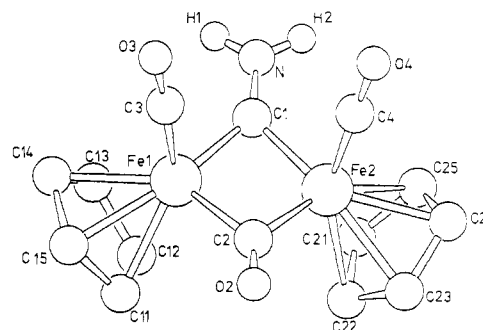
region is the $\nu(\text{NC})$ stretching frequency and which bands are the $\nu(\text{CO})$ vibrations³³ obviously extends to the $\text{M}(\text{CO})_5\text{CNH}$ series as well.^{33,34} For the same reason the assignments in case of $\text{Fe}(\text{CO})_2\text{CNH}(\text{diene})$ (5) might be questioned.³⁹ However, detailed IR and Raman studies both in solution and solid state of $[\text{Cr}(\text{CN})(\text{CO})_5]^-$ and **1a** including their ^{13}C -, ^{15}N -, and ^2H -labeled derivatives have now led to an assignment of the $\nu(\text{NC})$ modes to bands at 2100 s [Raman (CH_2Cl_2), $\text{NPr}^n_4[\text{Cr}(\text{CN})(\text{CO})_5]$] and 2026 m-s cm^{-1} [Raman (CH_2Cl_2), **1a**] as the most probable ones.^{51,52} In addition, ^{13}C , ^1H , and ^{15}N NMR data are now available of the hydrogen isocyanide ligand in **1a**, the former two displaying the expected triplet structure [$\delta(^{13}\text{C}, \text{CD}_2\text{Cl}_2) = 174.4$, $J(\text{C}, \text{N}) = 17.1$ Hz; $\delta(^1\text{H}) = 6.1$, $J(\text{H}, \text{N}) = 82\text{--}85$ Hz; $\delta(^{15}\text{N}, \text{solid}) = 145$ (rel $^{15}\text{NH}_4\text{Cl})$].⁵¹

The CNH ligand in **8** is fully substantiated by the doublets in the ^{15}N ($\delta = -172.4$ (rel MeNO_2), $^1J(^{15}\text{NH}) = 106$ Hz, -90°C) and ^1H NMR spectra [$\delta(\text{CNH}) = 11.45$, $^1J(\text{H}^{15}\text{N}) = 103$ Hz, -90°C] of a 98.8% ^{15}N -enriched sample.⁴²

Earlier, ^{14}N NMR data have been reported for **1a** [$\delta = -202$ (rel MeNO_2)], **1c** (-200), and **3a** (-218).⁵³

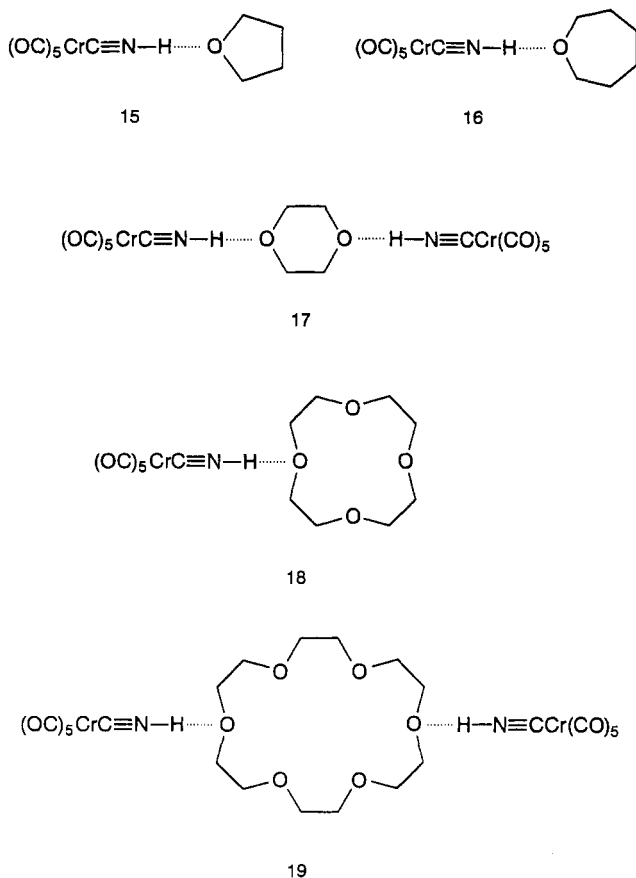
There is strong spectroscopic evidence for a unique oscillating $\mu\text{-}\eta^2\text{-CNH}$ ligand in **9** which formed on protonation of $\text{Mn}_2\text{H}(\mu\text{-}\eta^2\text{-CN})(\text{CO})_4(\text{dppm})_2$ without further structural rearrangement. Due to its ready uptake of CO (to give **8**), this first example of a CNH bridge could not be isolated, however.⁴² Protonation of $[\text{Fe}_2(\text{CN})\text{Cp}_2(\text{CO})_3]^-$, also carried out with the intention to arrive at a $\mu_2\text{-CNH}$ species, pursued a rather puzzling course (Scheme I).

Following the dynamics of this type of complexes (section II.B.3),⁵⁴ the initially formed CNH ligand moves into the bridging position, as desired. There, however, contrary to Deeming's system,⁴² its basicity is raised to such an extent that the monoprotonated form suffers an acid/base disproportionation, i.e., **11** is protonated



[W]CNH...FPP₅ is revealed by two intense broad IR bands at 2480 and 1750 cm⁻¹.³⁵ A series of similarly hydrogen-bonded 2:1 adducts between Cr(CO)₅CNH and acyclic diethers (dimethoxyethane, diethoxypropane, dipropoxyethane, etc.) has been described in the patent literature as early as 1964,⁶² though there were suggestions that these compounds were bisoxonium salts [(bidentate ether)·2H⁺][Cr(CN)(CO)₅]₂ containing the pentacarbonyl(cyano)chromate anion.³³

This view has clearly been disproved by the fortuitous discovery of the very stable and even sublimable (!) hydrogen-bonded Cr(CO)₅CNH...THF adduct 15 and the following directed syntheses of further adducts with cyclic ethers (16), diethers (17), and crown ethers (18, 19). In the case of 17, an N(H)...O distance of 2.877(11) Å was determined X-ray crystallographically, whose very small difference from the sum of the van der Waals radii of nitrogen and oxygen (2.93 Å) is indicative of only a weak H bond.⁶³



Much stronger hydrogen bonding has been expected and actually found in adducts of the (at least formally) symmetric type AHA⁻, 20 (A⁻ = [Cr(CN)(CO)₅]⁻), which formed on combining equimolar amounts of pentacarbonyl(hydrogen isocyanide)chromium and its conjugate base in an inert solvent. Naturally, in planning this experiment the authors have been guided by the exceptional strengths of the hydrogen bonds in the dihalides [Hal-H-Hal]⁻, and the far-reaching similarity between [Cr(CN)(CO)₅]⁻ and, particularly, Cl⁻. Striking spectroscopic peculiarities, speaking for the nature of 20 as an isolated *metal-stabilized hydrogen bisisocyanide ion*, are the highly characteristic ν(NC) absorption continuum superimposing the IR region from about 1800 to 300 cm⁻¹ (!) and the large downfield shift of the ¹H NMR signals of the hydrogen bridge protons,

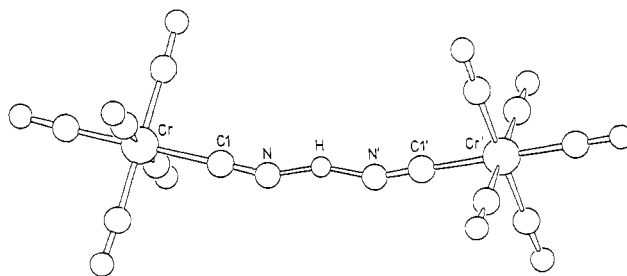


Figure 3. SCHAKAL drawing of the complex anion of 20a.⁶³

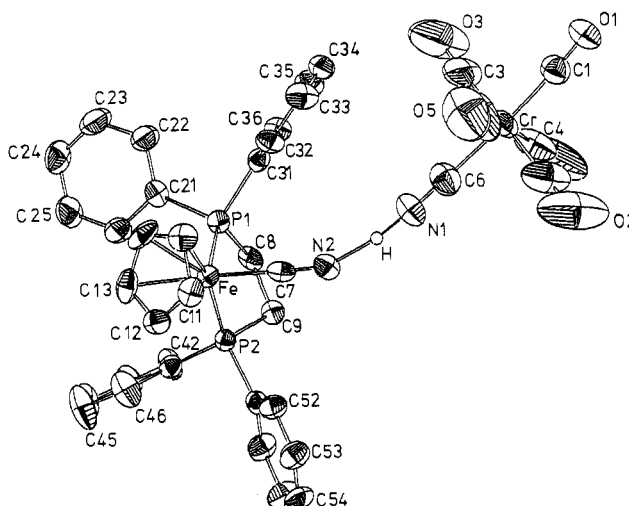
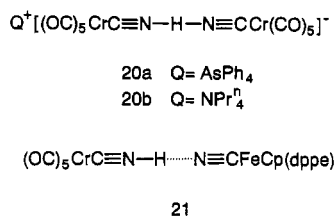


Figure 4. ORTEP drawing of 21.⁶³

findings which equally hold for the neutral CNHNC bridged adduct 21 prepared from Cr(CO)₅CNH and Fe(CN)Cp(dppe).⁶³



The presence in both compounds of strong "super-short" H bridge bonds with N...N' separations of only 2.569(7) Å (20a) and 2.557(12) Å (21), respectively, has been ascertained by X-ray structure analyses which, not unexpectedly, showed the H atom in 21 to be very asymmetrically positioned between the (CrC)N [1.17(14) Å] and N(CFe) atoms [1.40(14) Å] (Figures 3 and 4). However, in 20a, possessing crystallographic C₂ symmetry, the bridge H atom could not be localized with certainty, although a symmetric (nonlinear) bridge was the most likely. Here, unequivocal evidence in favor of a symmetric bridge (and, presumably, also a symmetrical single minimum potential for the motion of the proton) came from ¹⁵N-CPMAS NMR studies which revealed chemically equivalent cyano N atoms in 20a [δ = 205 (ext ¹⁵NH₄Cl)] while, surprisingly, two signals at δ = 219 and 185 have been observed in the case of 20b. Obviously, due to interactions with the counteranion, the average distances between the bridge H atom and the two nitrogen atoms are no longer identical.⁶³ From ¹⁵N-deuterium dipolar interactions observed in powder spectra, average N-D separations [1.13(1), 1.50(2) Å] have now been estimated which mount up to values about as different as the N-H ones in 21.⁶⁴

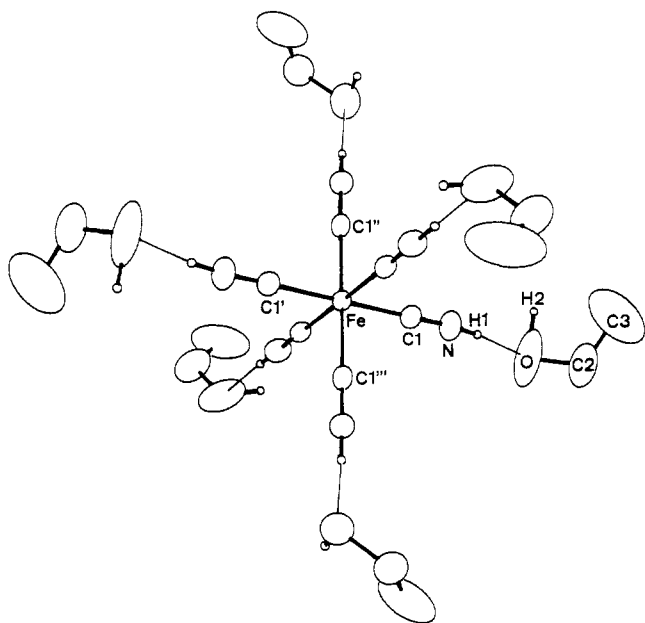
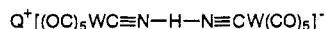
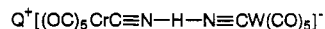


Figure 5. ORTEP drawing of the complex cation of 25.⁶⁵

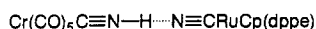
A new, much simpler access to **20** and other homodinuclear μ -hydrogen bisisocyanide complexes—careful addition of sulfuric acid to an aqueous solution of $\text{Na}[\text{Cr}(\text{CN})(\text{CO})_5]$ followed by addition of the respective cation—has recently been developed. Also, the new homo- and heterodinuclear members **22–24** have been synthesized.⁶⁴



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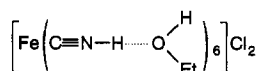


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24

An interesting link between the discrete dinuclear molecular and ionic H-bridged adducts of $\text{Cr}(\text{CO})_5\text{CNH}$ with O and N donors and the infinite 2- and 3-dimensional structures of the “cyanometallic acids” (see below) represents Buff’s “ferrocyanäthyl”. This nicely crystalline yet highly air-sensitive material, which had been obtained as early as 1854 by passing a stream of HCl through a solution of $\text{H}_4\text{Fe}(\text{CN})_6$ in ethanol has gone through various formulations throughout the decades. A low-temperature X-ray study of Buff’s compound now established the first example of a *homoleptic six-coordinate hydrogen isocyanide metal complex* (**25**). Its “supercomplex” cation consists of a central $[\text{Fe}(\text{C}-\text{NH})_6]^{2+}$ octahedron which is linked via six extremely short $[\text{N}\cdots\text{O} = 2.509(3) \text{ \AA}]$ and highly unsymmetrical $[\text{N}-\text{H} = 0.81(4); \text{H}\cdots\text{O} = 1.70(4) \text{ \AA}]$ hydrogen bonds to a second ligand sphere of six molecules of ethanol (Figure 5).⁶⁵ The authors regard **25** as a trapped



25

intermediate in the preparation of ethyl isocyanide (or ethyl isocyanide iron complexes), which, in fact, was

Buff’s original intention. To arrive at the final product, only a small shift of the bridging H toward the oxygen atom is required, followed by some rotary movement of the ethyloxonium part which brings the alkyl group near the isocyano nitrogen.⁶⁵ Actually, as has been shown later, this conversion is readily achieved by heating the reaction mixture.⁶⁶

Similar intermediates and introductory mechanistic steps may well be assumed in the novel hydroisocyanation reactions with CNH complexes discussed in section III.A,C and D.

These findings are contrasted by the large $\text{MCN}\cdots(\text{H})\text{N}^+$ separations found in the closely related systems of hexacyanometallates with polyammonium macrocyclic receptors, also termed “supercomplexes”,⁶⁷ e.g. $[\text{H}_8\text{L}][\text{Co}(\text{CN})_6]_2\text{Cl}_2\cdot 10\text{H}_2\text{O}$ ($\text{L} = 1,4,7,10,13,16,19,22,25,28$ -decaazacyclotriacontane). Interestingly, the anionic complex species does not go inside the macrocyclic cavity, and the strong bonding interactions are thought to be essentially Coulombic in nature.⁶⁸ Nevertheless, the second sphere coordination has been found to exert major effects e.g. on the redox properties and the photochemical reactivity of the $[\text{M}(\text{CN})_6]^{n-}$ anions.⁶⁹

Actually, there is considerable amount of evidence in the literature that many properties of coordinated cyanide (and through it, of the metal and the other ligands) are very sensitive to changes in the outer coordination sphere (“external” effects), e.g. to variations of the solvent, and that the observed effects are due to the strong tendency of coordinated CN to form H-bonds. Thus, H-bonding to coordinated cyanide in cobalt(III) corrinoids has expectedly been shown to reduce the electron density on the cyanide and hence its donor power to the metal, with further effects on both the cis and trans positions.⁷⁰

4. Coordination Polymers with CNHNC-Bridging Ligands

Vis à vis the novel metal-stabilized bisisocyanides **20–24** there exists a long known series of complex cyanide acids— $\text{H}_4\text{Fe}(\text{CN})_6$ was first reported in 1820⁷¹—which are obtained from the potassium salts either by ion exchange or by the hydrochloric acid ether method.^{10,72–74} The IR spectra of $\text{HAu}(\text{CN})_2$, $\text{H}_2\text{M}(\text{CN})_4$ ($\text{M} = \text{Pd}^{\text{II}}, \text{Pt}^{\text{II}}$), $\text{H}_3\text{M}(\text{CN})_6$ ($\text{M} = \text{Fe}^{\text{III}}, \text{Co}^{\text{III}}, \text{Rh}^{\text{III}}, \text{Ir}^{\text{III}}$), $\text{H}_4\text{M}(\text{CN})_6$ ($\text{M} = \text{Fe}^{\text{II}}, \text{Ru}^{\text{II}}, \text{Os}^{\text{II}}$), and $\text{H}_2\text{Fe}(\text{CN})_5\text{NO}$ and of several deuterated derivatives were measured and interpreted independently by three different research groups.^{75–77} Acids in which the number of protons equals half the number of cyanide groups showed a single sharp cyanide stretching band and an intense and extremely broad absorption, without pronounced structure and little effect due to deuteration, between 1900 and 600 cm^{-1} .⁷⁸ It was concluded that these acids contained symmetrical N–H–N hydrogen bonds, but that unsymmetrical N–H \cdots N bonds were present in the other acids. For the former type, also reasonable structures were proposed, i.e. infinite chains for $\text{HAu}(\text{CN})_2$, infinite sheets for $\text{H}_2\text{M}(\text{CN})_4$ ($\text{M} = \text{Pd}, \text{Pt}$) and a three-dimensional lattice based on linked octahedra for $\text{H}_3\text{M}(\text{CN})_6$ ($\text{M} = \text{Co}, \text{Rh}, \text{Ir}$).⁷⁵ Similar structures with $\text{MCN}\cdots\text{H}-\text{O}(\text{N})$ units have been suggested for hydroxonium and alkylammonium cyanometallates [e.g. $(\text{H}_3\text{O})_2[\text{Pd}(\text{CN})_6]$,⁷⁹ $(\text{NH}_2\text{Et}_2)_2-[\text{Pd}(\text{CN})_4]$ ⁸⁰]. X-ray and neutron diffraction studies

Table I. Selected Cyano(cyclopentadienyl) Complexes^a

[V(CN)Cp(CO) ₃] ^{-b,c} (60)	Cr(CN)Cp(CO)NO (57)	[Mn(CN)Cp(CO) ₂] ⁻ (42)	Fe(CN)Cp(CO) ₂ (43)	[Co(CN)Cp(CO)] ⁻ (27)
[V(CN) ₂ Cp(CO) ₂] ^{2--c}		[Mn(CN)Cp'(CO) ₂] ⁻ (40)	Fe(CN)Cp(CO)(PPh ₃) (44)	[Co(CN)Cp(PPh ₃)] ⁻ (28)
	[Mo(CN) ₂ Cp(CO) ₂] ^{-d}	[Mn(CN) ₃ Cp] ³⁻⁻ (41)	Fe(CN)Cp(dppe) (45)	[Co(CN) ₂ Cp] ²⁻⁻ (29)
	Mo(CN) ₃ Cp(CO) ₂		[Fe(CN) ₂ Cp(CO)] ⁻ (46)	[Co(CN) ₂ Cp] ⁻ (30)
	Mo(CN) ₃ Cp'(CO) ₂ } (37)		[Fe(CN) ₂ Cp(PPh ₃)] ⁻ (47)	[Co(CN) ₃ Cp] ⁻ (35)
	[Mo(CN) ₅ Cp] ²⁻⁻		[Fe ₂ (CN)Cp ₂ (CO) ₃] ⁻ (68)	Co(CN) ₂ Cp(PPh ₃) (36)
	[Mo(CN) ₅ Cp'] ²⁻⁻ } (38)			Co(CN)Cp(X)(CO) ^f
				(X = Br or I)
	Mo(CN)Cp(CO)NO (58)		Ru(CN)Cp(CO) ₂ (48)	
			Ru(CN)Cp(CO)(PPh ₃) (49)	Co(CN)Cp''(X)(CL) ^f
				(X = Br or I)
	W(CN)Cp(CO) ₃ ^d		Ru(CN)Cp(PPh ₃) ₂ (50)	
	[W(CN) ₂ Cp(CO) ₂] ^{-d}	Ru(CN)Cp(dppe) (51)		
	W(CN)Cp(CO)NO (59)		[Ru(CN) ₂ CpCO] ⁻	
	W(CN)Cp ₂ (OEt) ^e		Ru(CN)Cp(CO)CNMe	

^a Cp' = monomethylcyclopentadienyl; C'' = pentamethylcyclopentadienyl. ^b Reference 139. ^c Fischer, E. O.; Schneider, R. J. J. Chem. Ber. 1970, 103, 3684. ^d Reference 122. ^e Reference 35. ^f Morán, M. Z. Naturforsch. 1981, B36, 431.

which have been carried out on the free acids H₄Fe(CN)₆, H₃Fe(CN)₆, H₃Co(CN)₆ (including the deuteration), H₄W(CN)₈·6H₂O, and H₄W(CN)₈·4HCl·12H₂O show the deductions made from infrared spectroscopy to be essentially correct.^{81–86} In fact, while short [N...N = 2.68 [H₄Fe(CN)₆], 2.665(6) Å [H₃Fe(CN)₆]] although rather unsymmetrical N–H...N bridges [N–H, N...H = 1.23, 1.45 [H₄Fe(CN)₆]; 1.13, 1.62 Å [H₃Fe(CN)₆]] are present in the iron compounds, H₃Co(CN)₆ displays the third shortest [2.582(4) Å] intermolecular N–H...N hydrogen bond yet found which is either linear symmetric or statistically asymmetric with a double minimum potential; a model calculation suggests the latter.⁸⁷

B. "Organometallic" Cyano Complexes

Under this heading a rather arbitrary selection of cyano complexes has been made, guided mainly by expectations of their utility and suitability for organic transformations of CN (and of related ligands) in the coordination sphere of the metal. One might agree that for this purpose certain requirements should be met such as a good solubility in less polar aprotic media, the presence of further strongly bound (organic) ligands to guarantee a stable coordination sphere, and a relatively high electron density at both the metal and the cyanide, all in all characteristics which the term "organometallic" usually stands for.

Species such as [PtR₂(CN)₂]²⁻⁻ (R = Me, 2-thienyl, etc.),⁸⁸ [Pd(CN)_x(C₆R₅)_{4-x}]²⁻⁻ [R = H, x = 3; R = F, x = 1, 2 (cis and trans), or 3],^{89,90} and [Au(CN)_xR_y]⁻ (e.g. R = C₆F₅, x = 1, y = 1 or 3; x = y = 2)⁹¹ may be looked upon as prototypes; however, the cyano(η¹-organo)metallate family is comparatively small, and its chemistry has so far been restricted to the formation of cyanide-bridged oligomers. One also notes that the neutral members, Au(CN)R₂, are a priori tetranuclear with bridging CN groups (see section II.D). This is contrasted by the increasing number of cyano-η-cyclopentadienyl and carbonyl complexes described below in detail (section II.B.1 and 2), funds which have already been mobilized in a few isolated cases for applications in organic synthesis and catalysis, yet definitely lack a systematic study of their chemical potential.

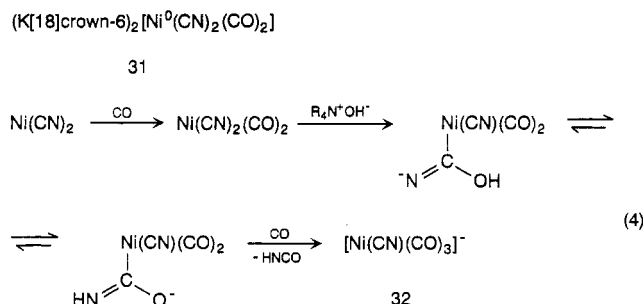
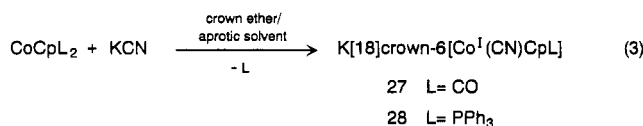
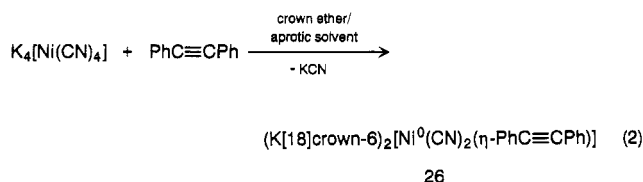
On the other hand, many a classical Werner-type complex like [Fe(CN)₆]⁴⁻⁻, M(CN)₂(bipy)₂ (M = Fe, Ru, Os),⁹² or [Au(CN)₂]⁻, and "borderline cases" such as

cyanophosphine complexes^{8,93} [e.g. Pt(CN)₂(PR₃)₂⁹⁴ or *trans*-Pt(CN)(X)(PPh₃)₂ (X = Cl, Br, I)⁹⁵] have turned out to be perfect starting materials for the investigation of a [M]CN chemistry (sections III.A and D), yet are not particularly dealt with in this chapter. This is equally true of the "bioinorganic" cyano cobaloximes, Co(CN)(dmgH)₂L,⁹⁶ and related Schiff base model compounds.⁹⁷ The reactions discussed in part III are thus of rather universal application to a wide variety of cyano complexes.

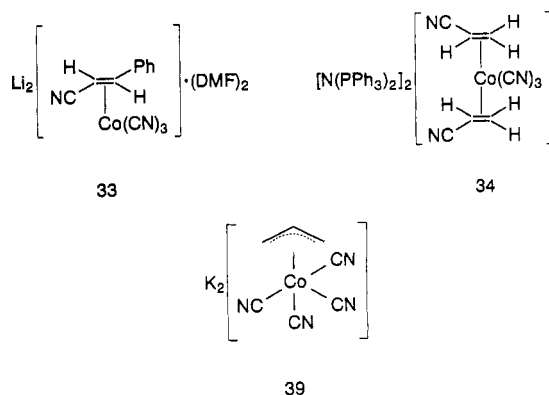
1. Low-Valent Cyano and Cyano-η-cyclopentadienyl Complexes

The chemistry of low-valent organocobalt and nickel cyanides 26–30 has recently been developed by Carter and Stuhl using a crown ether strategy (eq 2) which permits carrying out in aprotic organic solvents reactions, e.g. of K₄[Ni(CN)₄] or K₄[Ni₂(CN)₆], that previously required liquid ammonia as a solvent.^{98,99} The same strategy has been applied for a high-yield straightforward synthesis of 27 and 28 (eq 3), and crown ether-derived stationary phases [e.g. (K[18]-crown-6)CN-silica] have been used for their separation.¹⁰⁰ Concerning the reactions of these particularly low-valent compounds, however, cyanide had turned out to be more or less a mere spectator ligand, and the "discovery of the nongenerality of electrophilic attack on coordinated cyanide" has been set forth.^{101,102} Although this was certainly disappointing from the standpoint of organometallic synthesis (however, compare with section III.A) it has been pointed out that here cyanide plays a special role in providing competitive electron-transfer reaction pathways for 27–30 (Table I) and catalytic activities for 26 (trimerization of terminal alkynes) and 31 (carbonylation of benzyl bromide) with new hopes for organic synthesis.^{103,16} Cyanonickel(II) species, too, have been reported to catalyze carbonylations e.g. of allyl halides to carboxylic acids under phase-transfer catalysis conditions, and the key catalytic species was believed to be [Ni(CN)(CO)₃]⁻ (32). A possible mechanism for the conversion of nickel cyanide to 32 is nucleophilic attack by hydroxide at the cyanocarbon (eq 4), much in analogy to Hieber's base reaction.¹⁵

Most of these findings are, of course, to be seen in relation to [Co(CN)₅]³⁻⁻, a long-known homogeneous catalyst and highly valuable reagent in organic chemistry, yet without a propensity for reactions at the



coordinated CN (see, however, ref 104).^{17,105–108} Through the use of tetraalkylammonium cations an extensive characterization of $[\text{Co}(\text{CN})_5]^{3-}$ and other cobalt-cyanide complexes was possible both in aprotic solvents and in the solid state.^{106,109,110} More recently, Funabiki et al. had realized and widely exploited the catalytic capabilities of $[\text{Co}^{\text{I}}(\text{CN})_4]^{3-}$ in aqueous solution both for cyanations of vinyl halides and hydrocyanations/hydrogenations of alkynes.^{111,112} In an effort to establish an identical chemistry in aprotic systems,¹¹³ Stuhl et al. managed to isolate (and structurally characterize) square-planar $[\text{N}(\text{PPh}_3)_2]_2[\text{Co}(\text{CN})_4]$ along with some (η -alkene)cyanocobalt(I) species tentatively formulated as 33 and 34.^{114,115}



A similar though largely unutilized potential for organic syntheses and catalyses appears to exist in the various phosphine and diphosphine derivatives of low-valent cobalt, rhodium, and nickel cyanides described earlier by Rigo et al.¹¹⁶

At about the same time, Pauson and Dineen had reported on the preparation of high-valent polycyano-(organo)cobalt (35, 36) and -molybdenum compounds (37, 38) from the corresponding carbonyl iodides and potassium cyanide (Table I).^{117,118} While in $\text{MoCpI}_3(\text{CO})_2$ cyanide replaces first the halide and then the carbonyl group, there is evidence for the reverse order substitution/metathesis in $\text{CoCpI}_2(\text{CO})$. Besides, *direct* routes to 35 and 36 as well as to (allyl)cobalt(III)

cyanides (e.g. 39) were provided by reactions of the appropriate carbonyl precursors $[\text{CoCp}(\text{CO})_2]$, $\text{CoCp}(\text{CO})\text{PPh}_3$, $\text{Co}(\eta\text{-C}_3\text{H}_5)(\text{CO})_3$ with cyanide in air or in mixtures with iodine, respectively.¹¹⁹ Analogous mixed cyano(cyclopentadienyl)carbonylcobalt(III) species, $\text{Co}(\text{CN})\text{Cp}(\text{X})\text{CO}$ and $\text{Co}(\text{CN})(\eta\text{-C}_5\text{Me}_5)\text{X}(\text{CO})$, had been obtained by oxidative addition of XCN ($\text{X} = \text{Br}$ or I) to the parent dicarbonyls. In contrast, photolysis in the presence of CN^- accomplished substitution of one (40) or all three CO groups (41) in (methylcyclopentadienyl)tricarbonylmanganese while maintaining the oxidation state +I of manganese.¹¹⁸ Earlier, $\text{MnCp}(\text{CO})_3$ had been irradiated together with NaCN and shown to give 42.³⁶

A series of iron(II) and ruthenium(II) species 43–51 (Table I) the phosphine derivatives of which are particularly electron rich and actually proved to be first-rate candidates for reactivity studies (see, e.g. section III.D) has been synthesized by metathetical reaction of the respective halogeno complexes with KCN .^{120–126}

Of the infinitely small number of arene-cyano complexes only one, $[\text{Cr}(\text{CN})(\eta\text{-arene})(\text{CO})_2]^-$, has come into prominence as precursor of chiral acyl isocyanide complexes which have successfully been tested in both asymmetric organic synthesis and catalysis (cf. section III.A.2).^{36,127,128} A second specimen, the isoelectronic neutral $\text{Mn}(\text{CN})(\text{CO})_2(\eta\text{-C}_6\text{H}_3\text{Me}_3)$, is worth mentioning primarily for its peculiar way of formation by rearrangement on refluxing an aqueous suspension of the 1-cyano-2,4,6-trimethylcyclohexadienyl compound $\text{Mn}(\text{CO})_3(\eta^5\text{-C}_6\text{H}_3\text{Me}_3\text{CN})$ —unexpected product of an intended metathetical reaction between $[\text{Mn}(\text{CO})_3(\eta\text{-C}_6\text{H}_3\text{Me}_3)]\text{I}$ and KCN .¹²⁹

2. Carbonylcyanometalates. The "Silazid" Method

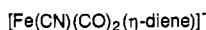
A very elegant and now widely used entry into cyanocarbonylmetalates—the main body of "organo-metallic" cyano complexes—involves treatment of the parent metal carbonyls with sodium bis(trimethylsilyl)amide ("silazid"). In this reaction which was discovered by Wannagat and Seyffert, nucleophilic attack by $\text{N}(\text{SiMe}_3)_2^-$ occurs at the carbon atom of a CO ligand and is followed by elimination of hexamethyldisiloxane thereby leading to a substitution of the carbonyl oxygen (through formally N-) without breakage of the metal-carbon bond (eq 5).¹³⁰ The X-ray structure of tetra-



carbonyl(cyano)ferrate [as bis(triphenylphosphine)iminium salt] has been determined and found to be a distorted trigonal bipyramid with the cyanide in an axial position as predicted from a simple π -bonding model.¹³¹

The same reaction was later applied by King to synthesize the pentacarbonylcyanometalates of chromium, molybdenum, and tungsten, $\text{Na}[\text{M}(\text{CN})(\text{CO})_5]$,³³ yet it was H. Behrens who actually explored the scope of this method by converting many different mononuclear metal carbonyl derivatives into the corresponding anionic mixed-ligand monocyano complexes 52–56.^{132–137} Also, $\text{M}(\text{CN})\text{Cp}(\text{CO})\text{NO}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) (57–59) and $\text{K}[\text{V}(\text{CN})\text{Cp}(\text{CO})_3]$ (60) have been prepared in the same manner.^{138,139} It is of great advantage that

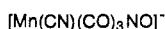
these reactions can be carried out in organic solvents which very much facilitates the isolation and purification of the mostly air-sensitive products. Moreover, for quite a number of these compounds, this procedure is absolutely indispensable: neither the olefin nor the halogenocyano complexes would have been accessible by reaction of the parent metal carbonyl derivatives with KCN due to the substitution of these ligands by CN^- . One has to be aware, however, that in several cases $\text{NaN}(\text{SiMe}_3)_2$ acts as a strong base, i.e. deprotonation of CH acidic ligands is observed instead of $\text{CO} \rightarrow \text{CN}^-$ transformation, a variant which proved similarly profitable in organometallic synthesis.¹³²



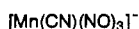
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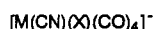
53 M = Mn, Re



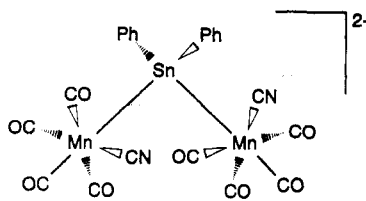
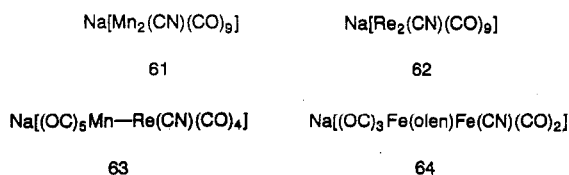
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56 $\begin{cases} \text{M} = \text{Mn, Re} \\ \text{X} = \text{Cl, Br, I} \end{cases}$

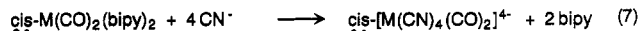
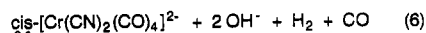
Conversion of only one CO ligand to give the monocyano complexes 61–64 is also characteristic of the dinuclear metal carbonyls $\text{Mn}_2(\text{CO})_{10}$, $\text{Re}_2(\text{CO})_{10}$, and $\text{MnRe}(\text{CO})_{10}$, as well as of the olefin-bridged species $(\text{OC})_3\text{Fe}(\text{olen})\text{Fe}(\text{CO})_3$ (olen = cyclooctatetraene, 1,1'-di-2,4-cyclohexadienyl, 1,1'-di-2,4-cycloheptadienyl).^{140,132} In 61–63, the cyano ligands occupy axial positions. In contrast, two equatorial (cis) CN^- ligands, one at each manganese atom, are generated in their reactions of the EPh_2 -bridged complexes $\text{Ph}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$ and $\text{Ph}_2\text{Pb}[\text{Mn}(\text{CO})_5]_2$ with bis(trimethylsilyl)amide (1:2) (cf. 65).¹⁴¹



65

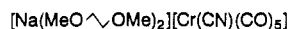
Prior to the advance of this method, carbonylcyanometallates have been obtained from various metal carbonyl derivatives and the cyanide ion. In this field, acknowledgement must be made of the pioneering work of Behrens who synthesized numerous mono to tetra-cyanometallates of groups 6 and 7 both by oxidation of $[\text{Cr}^{\text{II}}(\text{CO})_5]^{2-}$ with aqueous solutions of KCN (e.g. eq 6) [or with $(\text{CN})_2$ or ICN]¹⁴² and by direct substitution reactions of the parent carbonyls or of bipy or phosphine derivatives carried out in liquid ammonia (eq 7).¹⁴³

$\text{Na}[\text{Cr}(\text{CN})(\text{CO})_5]$, too, was first synthesized by oxidation of $\text{Na}_2[\text{Cr}^{\text{II}}(\text{CO})_5]$ in 1959.¹⁴⁴

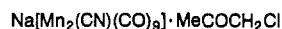


(M = Cr, Mo, W)

A much simpler and more efficient preparation of a series of alkali metal bidentate ether complex salts of $[\text{Cr}(\text{CN})(\text{CO})_5]^-$, e.g. 66, viz. heating chromium hexacarbonyl together with sodium cyanide in the noncyclic diether, has been described in a patent.¹⁴⁵ Similar solvates, e.g. 67, have been encountered in connection with reactivity studies on sodium nonacarbonylcyanodimanganate.¹⁴⁶



66



67

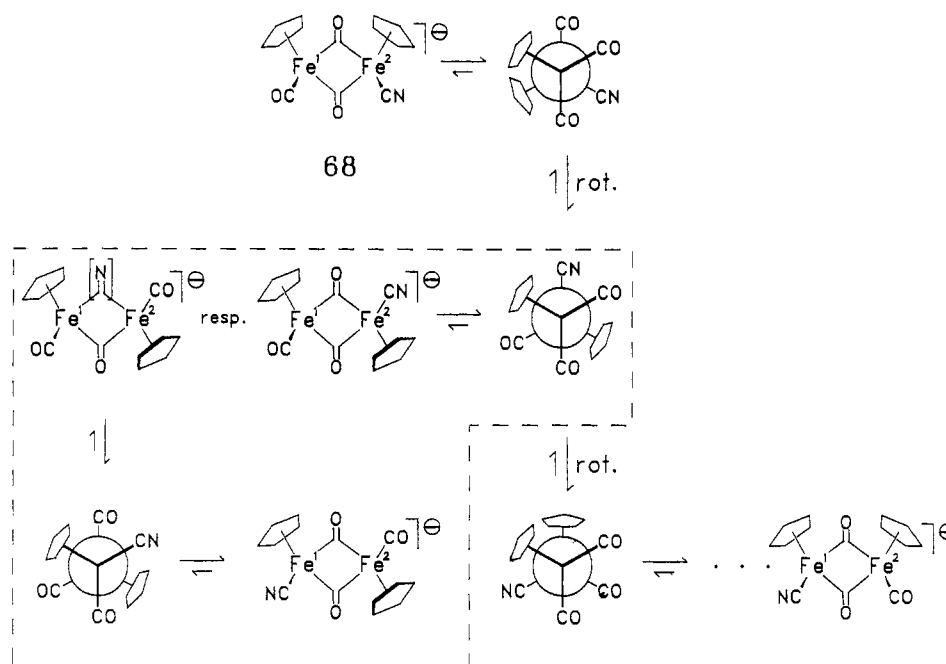
The deep-green paramagnetic $\text{Cr}^{\text{I}}(\text{CN})(\text{CO})_5$ ¹⁴⁷ which has been reported to result from deep-blue $\text{Cr}^{\text{I}}(\text{I})(\text{CO})_5$ and ICN deserves special attention, and further investigations are highly desirable in view of more recent electrochemical and ESR findings on $[\text{Cr}^0(\text{X})(\text{CO})_5]^- / \text{Cr}^{\text{I}}(\text{X})(\text{CO})_5$ species (X = Hal, CN) and the assumed intermediacy of $\text{Cr}^{\text{I}}(\text{CN})(\text{CO})_5$ in the "radical alkylation" reactions (see section III.B.1).^{148–150} In this context, mention should also be made of a particularly careful study of the redox chemistry of $\text{Na}[\text{Mn}(\text{CN})\text{Cp}(\text{CO})_2]$ and the CN-bridged dinuclear complexes $[\text{Cp}(\text{OC})_2\text{MnCNMn}(\text{CO})_2]^-$ and $[\text{Cp}(\text{OC})_2\text{MnCNW}(\text{CO})_5]^-$ from which, however, none of the hoped for odd electron count species could be obtained.¹⁵¹ By way of contrast, single-electron oxidation reactions of various phosphine- and phosphite-substituted mononuclear cyanomanganese(I) [e.g. $\text{Mn}(\text{CN})(\text{CO})_2\{\text{P}(\text{OPh})_3\}(\text{dppm})$] as well as cyanide-bridged dimanganese(I), manganese-ruthenium, and manganese-rhodium systems have successfully been investigated and found to frequently induce cis-trans isomerization (cf. section II.D).^{47,152–154}

Low-valent pentacyanometallates of chromium, manganese, and iron with isoelectronic π -acceptor ligands (CO , NO^+) have recently been reviewed.¹⁵⁵

3. Cyanoclusters?

Thermal or photochemical activation of a metal-CO bond in the presence of cyanide now is the method of choice for the synthesis of cyano-substituted derivatives including dinuclear CN-bridged specimen, e.g. $[\text{Fe}_2(\text{CN})(\text{CO})_8]^-$, $[\text{W}_2(\text{CN})(\text{CO})_{10}]^-$ (cf. II.D),¹⁵⁶ and the "probably dinuclear" complex $(\text{NEt}_4)_4[\text{V}(\text{CN})_2(\text{CO})_4]^{2-}$.¹⁵⁷ The use of large organic cations such as $\text{N}(\text{PPh}_3)_2^+$, first introduced by Ruff, allows one to conduct the reactions homogeneously, at the same time facilitating the workup procedure and stabilizing the products.¹⁵⁶ A combination of these strategies has been employed to get a hold of the "minicluster" $[\text{Fe}_2(\text{CN})\text{Cp}_2(\text{CO})_3]^-$ (68).¹⁵⁸ Actually, cyano clusters have rarity value; on

Scheme II. Coupled Cis \rightarrow Trans Isomerization and Terminal \rightarrow Bridge \rightarrow Terminal Migration of the CN Ligand in 68



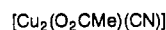
the other hand, they are of particular interest due to the availability for the cyano ligand (or its eventual reaction products) of both terminal and (μ -C,C)-bridging positions with very different implications for the stereochemistries and reactivities of the respective groups (cf., e.g. sections II.A.2 and III.A.2). The X-ray structure analysis of the $N(PPh_3)_2^+$ salt shows a cis-configured complex anion with long C–O distances in the bridge and a cyano ligand which is disordered between the two terminal positions. In solution, however, a temperature- and solvent-dependent equilibrium exists between the more stable cis and the trans complex which is superimposed by an unprecedented CN migration between the iron centers via the bridging position (Scheme II).

The only known simple cyanocarbonyl cluster deserving this designation is Deeming's $[N(PPh_3)_2][Os_3H_2(CN)(CO)_{10}]$ which, however, only exists in solution as a mixture of three main isomers plus a fourth in traces. In all four isomers the cyanide ligand is thought to just occupy *terminal* sites although, in principle, bridging positions are available and obviously taken up by the protonation products (section II.A).⁵⁷ In contrast to that, in the before-mentioned metal-metal-bonded cyanodimanganese, -dirhenium, and -manganese-rhenium systems (61–63), the CN group is restricted to a terminal (axial) position. Restriction of the CN groups to (μ -C,N)-bridging modes as in the clusters $Mn_4Pd_4(\mu-CN)_4$ and $Ru_6(\mu-CN)_2$ (see section II.D) also appears to preclude a CO-like chemistry of cyanide.^{159,160}

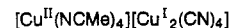
4. Cyano Ligands from Other Sources

The "special relations" between Cu^I or Cu^{II} and cyanide that are obvious already from the structural variety of their coordination compounds¹⁶¹ seem to also effect a wide range of use in organic syntheses. A more recent example concerns diverse cyanocopper complexes, e.g. 69–71, each of which turned out to be

extremely active in the cyanation of certain aryl halides, and a mechanism involving concerted nucleophilic substitution *within the coordination sphere of Cu^I* was proposed. Interestingly, these complexes are formed when either copper(I) acetate or copper(II) acetate reacts with formamide in the presence of acetic anhydride as dehydrating agent.^{162,163} Another precursor to



69



70



71

cyanide was formaldoxime; copper compounds derived thereof, e.g. the mixed-valence complex $[Cu_3(O_2CMe)_5(MeCONH_2)(CH_2NOH)_2]$, cause the cyanide substitution in aryl halides at room temperature.^{164,165} Also note, that the cyanide ligand in $Cu_5(CN)_6(dmef)_4$ originates from diaminomaleonitrile, an HCN tetramer, which has oxidatively been fragmented by the action of cupric acetate.¹⁶⁶ On prolonged air oxidation, a very similar fragmentation occurred in the ligand sphere of a bis(diiminosuccinonitrile)cobalt(II) dimer to produce a cyanocobalt(III) moiety.¹⁶⁷

Cyano and/or ethoxycarbonyl ligands have been introduced into complex frameworks using ethyl cyanoformate as starting material, and it is generally agreed that these reactions proceed through oxidative addition, i.e. reductive cleavage of the C–C bond occurs at the low-valent metal to give cyano/ethoxycarbonyl [e.g. $Ni(CN)(CO_2Et)\{MeC(CH_2PPh_2)_3\}$]^{168,59} or dicyano complexes [e.g. *trans*- $Pt(CN)_2(PPh_3)_2$].⁹⁵ Introduction of HCN into several triphenylphosphine complexes of rhodium(I) and iridium(I) clearly proceeds by oxidative addition as does formation of $Ni(CN)_2(PPh_3)_2$ from $Ni(CO)_2(PPh_3)_2$ and cyanogen, or of $Ni(CN)(Ph)(PCy_3)_2$ from $Ni(\eta-C_2H_4)(PCy_3)_2$ and benzonitrile.^{169–171} $[Ni^{II}(CN)(Et)(\eta-C_2H_4)P(O-o-Tol)_3]$ has been prepared from

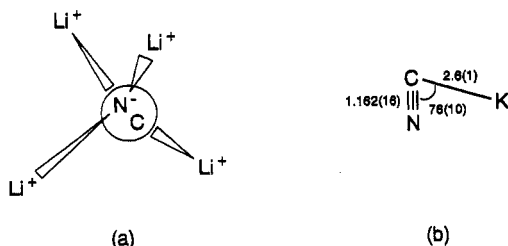


Figure 6. "Coordination sphere" of CN^- in solid LiCN (a) and T-shaped molecular structure of gaseous KCN (b).

$\text{Ni}^0(\eta\text{-C}_2\text{H}_4)\{\text{P}(\text{O}-o\text{-Tol})_3\}_2$, HCN , and C_2H_4 at -40°C and recognized as the active intermediate in the catalytic hydrocyanation of ethylene.¹⁷² A similar although intramolecular redox process appears to be operative in the slow rearrangement of $\text{Pt}^0(\eta\text{-NCC}\equiv\text{CCN})(\text{PPh}_3)_2$ into $\text{cis-Pt}^{\text{II}}(\text{CN})(\text{C}\equiv\text{CCN})(\text{PPh}_3)_2$.¹⁷³ Conversely, (acyl)cyanonickel species have been identified in carbonylation studies of the complexes $\text{Ni}(\text{CN})(\text{Ph})\text{L}_2$ (L = various phosphines) and found to undergo reductive elimination of PhCOCN in the presence of excess CO .¹⁷⁴

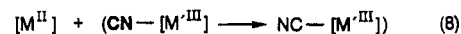
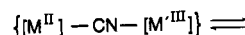
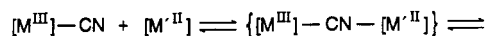
Dealkylation of isocyanides, i.e., the reverse of the well-known alkylation of metal cyanides to give isocyanide complexes (cf. section III.A.1) occurs occasionally and unexpectedly. It has been reported, for example, for methyl isocyanide iron(II) and platinum(II) complexes;^{175,176} however, the most ready source for the CN ligand appears to be *tert*-butyl isocyanide^{177,178} which has even been employed for (hydro)cyanations in organic synthesis.¹⁷⁹ Cyano complex formation from $\text{Ru}(\text{Cl})\text{CpL}_2$ (L = CO , PPh_3) and R_3BCN^- (R = H , Ph) (via the "cyano-bridged" species $[\text{Ru}]\text{-NC-[B]}$ and $[\text{Ru}]\text{-CN-[B]}$) seems closely related (cf. 48 and 50, Table I).¹²³

C. Isocyano Complexes and $\text{CN} \rightleftharpoons \text{NC}$ Isomerizations

Even though alkali cyanides are occasionally referred to as "isocyanides" due to the closer neighborhood of M^+ to the nitrogen atom of CN^- both in the crystal lattice (see, e.g. Figure 6a)^{161,180} and in geometry-optimized gaseous ion pairs¹⁸¹ and in spite of the fact that microwave experiments have shown NaCN and KCN to possess triangular (" π -type") equilibrium structures (Figure 6b) in the gas phase,^{182,183} there is general agreement, that the common mode of cyanide attachment to metals and metalloids is *monohapto* via carbon.³ It should be kept in mind, however, that unambiguous proof of this assumption only exists for those cyanides and cyano complexes [e.g. $\text{Hg}(\text{CN})_2$,¹⁸⁴ $[\text{Co}(\text{CN})(\text{NH}_3)_5]\text{Cl}_2$,¹⁸⁵ and $\text{Cs}_2\text{K}[\text{Cr}(\text{CN})_6]$ ¹⁸⁶] on which particularly precise X-ray structure analyses or, preferentially, neutron diffraction experiments have been carried out.¹⁸⁷

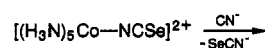
Still, the "Ambident Nature of Cyanide" is common knowledge,³ and much evidence has been accumulated in the last 2–3 decades concerning the existence of linkage isomers of cyanide in coordination compounds. The *isocyano* complexes $[\text{Co}(\text{CN})_5\text{NC}]^{3-}$ and $[\text{Cr}(\text{NC})(\text{H}_2\text{O})_5]^{2+}$ were postulated as transient intermediates formed by "remote attack" of the reductant in the inner-sphere portions of the reactions of $[\text{Co}^{\text{III}}(\text{CN})(\text{NH}_3)_5]^{2+}$ [or *trans*- $[\text{Co}^{\text{III}}(\text{CN})(\text{NH}_3)_4\text{H}_2\text{O}]^{2+}$, *cis*- $[\text{Cr}^{\text{III}}(\text{CN})_2(\text{H}_2\text{O})_4]^+$, etc.] with $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ and

$\text{Cr}^{2+}(\text{aq})$, respectively.^{188–190} This was chemically plausible as the "products of their disappearance" were the isomeric *cyano* complexes, yet much stronger support came from the absorption spectra which were consistent with the expected lower ligand field strength of the N-bonded cyanide.¹⁹¹ Using the well-established sequence of precursor complex formation, electron transfer, and successor complex dissociation, one arrives at a general mechanism for this type of *CN-mediated* redox reactions which at the same time provides a general kinetic route for the synthesis of *isocyano* species 72 (eq 8).¹⁹²



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Other short-lived isocyano intermediates $[[\text{Cr}(\text{NC})(\text{CO})_5]^-]$, $[\text{Ru}(\text{NC})(\text{NH}_3)_5]^+$ have been claimed as primary products in deprotonations of the respective HCN complexes.^{34,24} Likewise, oxidative desulfurization (thermal deselenation) of the isothiocyanato (isoselecyanato) ligand, e.g. in $[\text{Co}(\text{NCS})(\text{NH}_3)_5]^{2+}$ or $[\text{Pd}(\text{NCS})(\text{dienEt}_4)]^+$ ("oxidative substitution") ($[\text{FeCp}(\text{NCSe})(\text{CO})\text{PPh}_3]$), to give the corresponding cyano complex is thought to proceed via the unstable isomer.^{193,194} A similar selenium extrusion reaction (eq 9)



has now led to the isolation of the surprisingly stable $[\text{Co}(\text{NC})(\text{NH}_3)_5]^{2+}$ as a yellow-orange crystalline nitrate perchlorate which eventually rearranges quantitatively yet *very slowly* (hours, 25°C) to $[\text{Co}(\text{CN})(\text{NH}_3)_5]^{2+}$. Again, the visible spectra of both isomers are diagnostic of the CoN_6 ($\lambda_{\text{max}} = 459\text{ nm}$) and CoN_5C skeletons ($\lambda_{\text{max}} = 438\text{ nm}$), respectively.¹⁹⁵ Also note that the bridging NCS group in $\text{Rh}_2(\mu\text{-NCS})(\mu\text{-CO})_2(\mu\text{-dppm})_2$ has been converted into a $\mu\text{-}\eta^1, \eta^2\text{-CN}$ ligand by reaction with CO (see section II.D).¹⁹⁶

There are two more—although not undisputed—reports on isolated cobalt(III) complexes containing monodentate isocyano ligands along with en and trien chelating groups. One is on diisocyano species to which the structures 73a,b have been assigned on the basis of IR ($\nu(\text{NC})$ 2125–2140 cm^{-1}) and vis/UV spectra (Figure 7).¹⁹⁷ Both, the ease of formation of 73a,b (on simply reacting suitable acetato complex precursors with NaCN) and their obvious stability can be understood in terms of Jørgensen's concept of *symbiosis* which depicts the tendency of flocking together of like ligands—here of *six* N-bonded groups—in a complex.¹⁹⁸

$\text{Co}(\text{NC})(\text{dmgH})_2(\text{H}_2\text{O})$ is the only claimed isocyano complex whose structure had been determined by X-ray analysis;^{199,200} nevertheless, it is this one of all examples which has clearly been disproved recently.²⁰¹ The compound was reported to photolytically and/or thermally rearrange to the cyano isomer, a process which had been followed by IR ($\nu(\text{NC})$ 2136; $\nu(\text{CN})$ 2186 cm^{-1}).

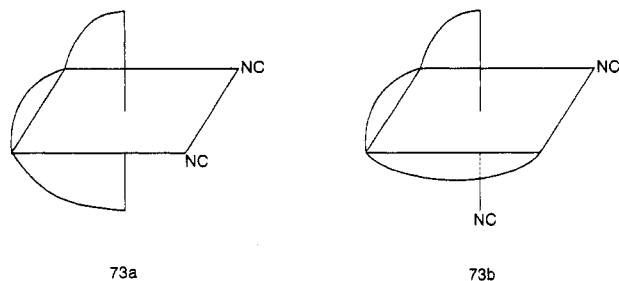


Figure 7. Postulated isocyano isomers *cis*- α -[Co(NC)₂(trien)]ClO₄ (**73a**) and *cis*- β -[Co(NC)₂(trien)]ClO₄ (**73b**) (trien = triethylenetetramine) from the reactions of [CoX₂(trien)]ClO₄ (X = CHCl₂CO₂ or MeCO₂) with NaCN in water.

A redetermination of the X-ray crystal structure and IR spectroscopic reasoning now convincingly disclosed that Co(NC)(dmgH)₂(H₂O) is simply the cyano complex Co(CN)(dmgH)₂(H₂O) and that the material obtained from heating it probably was a polymeric cyano-bridged species.²⁰⁰ For their attempted synthesis of isocyano-cobalt complexes, Alvarez and Lopez made use of the strategy of temporary blocking the C end of CN⁻ by a Lewis acid—here Ag⁺—in order to force Co–N coordination, a trick by which actually dozens of other cyano/isocyano isomers had been synthesized at metals, metalloids, and organic substrates.^{24,202} We also note that this strategy had already displayed its strength way back in 1856, when Lieke, Meyer, and Gautier obtained the very first isocyanides from AgCN and RI, and that it is ultimately inherent in the authors' syntheses of functional isocyanides, e.g. from [Cr(CN)(CO)₅]⁻ (see sections III.A.1 and 3).^{203–205} Moreover, the addition of Ag⁺ (Hg²⁺) ions to cyanochromium(III) complexes in aqueous solution obviously promotes cyano \rightarrow isocyano linkage isomerizations of the type CrC \equiv NAg \rightarrow CrN \equiv Cg (μ-CN-“flip”)²⁰⁶ although isocyano silver complexes, e.g. [Ag(CN)(NC)]⁻, have been discussed in liquid ammonia.²⁰⁷ Linkage isomerization of bridging cyanide has also been reported for polymeric materials, particularly of the kind of Prussian Blues,^{191,208,209} as simple binuclear models, pairs of μ-CN linkage isomers (**74** and **75**) could be prepared, isolated, and structurally characterized or, at least, “isolated and characterized in solution”.^{210,211} In recent years, solid-phase thermal deaquation-anation of double-complex salt precursors has proven an efficient method for the preparation of such species.²¹²



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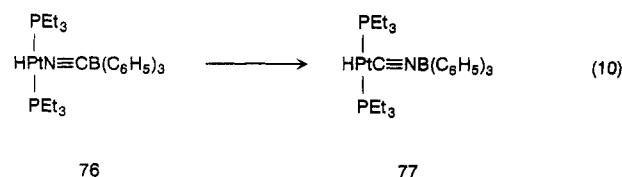


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The organometallic chemist's entry into cyanide chemistry was accompanied by a lasting controversy on the nature, cyano or isocyano, particularly of organosilicon and -germanium derivatives which, however, has meanwhile been settled.²¹³ Thus, the bewildering formation of “isocyanide products” such as R₃SiNCS or R₃SiNCF₃(CO)₄ upon reaction of Si(CN)R₃ with sulfur or Fe(CO)₅, respectively, is explained by

the relative lability of the polar E–CN bond and a tendency for isomerizations of the kind EC \equiv NM \rightarrow EN \equiv CM. Moreover, there is convincing evidence for the presence of small amounts of R₃SiNC in equilibrium with the cyano form (see, however, ref 214).²¹⁵ Actually, a comparatively long-lived intermediate was observed in the reaction of MnCp(CO)₂THF with Si(CN)Me₃ and identified as MnCp(CO)₂NCSiMe₃, while at group 6 metal carbonyls the same isomerization Me₃SiCN \rightarrow Me₃SiNC must be rapid.^{45,50} There is also a report on a series of mono-, bis-, and even trisorganosilyl and -germyl isocyanide (yet obviously *no* cyanide) derivatives of the latter system; of Mo(CO)₅CNGePhMe₂, the structure has been determined.⁴⁶

In the related case of boron, Na⁺BH₃NC⁻ was isolated and spectroscopically identified (IR, ¹¹B NMR) in 1:4 mixtures with the “normal” salt reflecting an increased stability of the isocyano ligand at this main group element.^{216,217} The isocyano \rightarrow cyano interconversion was found to be H⁺ and CN⁻ catalyzed,²¹⁶ and an activation energy of only 29 kcal mol⁻¹ was estimated for the unimolecular rearrangement.²¹⁸ Surprisingly, neither BH₃CN⁻ nor BPh₃CN⁻ showed any tendency to isomerize to the “B-isocyanide” when reacting with group 6 metal hexacarbonyls in boiling glyme, the only product being the N-bonded [M(NCBR₃)(CO)₅]⁻.²¹⁹ In fact, this appears to be the general mode of coordination of cyanoborates to the usual metal ions.²²⁰ At ruthenium(II) or platinum(II) in more “organometallic” envelopes, however, a different situation is encountered; now the nitrile derivatives RuCp(NCBR₃)L₂ (L = CO or PPh₃, R = H or Ph) and **76** are found to rearrange, readily affording the isonitrile species RuCp(CNBR₃)L₂ and **77**, respectively (eq 10).^{123,221}



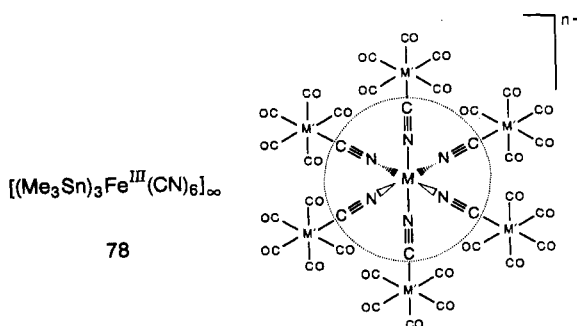
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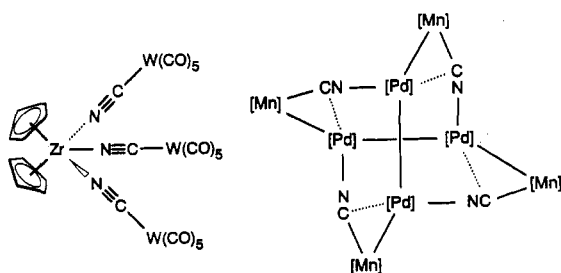
D. Cyano-Bridged Complexes

Contrary to CO, bridging of metals by CN⁻ almost exclusively occurs in a more or less linear [M^B]-C \equiv N[M^A] fashion; a coordination polymer consisting of an infinite three-dimensional network of this pattern is among the very first chemicals synthesized by man, viz. the paint “Berliner Blau” (or Prussian Blue), already mentioned, in 1710.²²² The cubic face-centered structural model originally proposed by Keggin and Miles²²³ for Prussian Blue and its analogues M^A_m[M^B(CN)₆]_n·xH₂O^{2,3,10,224} has later been modified mainly by Ludi in such a way that a certain number of M^B(CN)₆ sites was vacant and these vacancies were randomly distributed. The water molecules appear partly coordinated to M^A at empty nitrogen sites, partly zeolitically contained in the holes of the relatively open framework.^{7,225,226} Today, Prussian Blues (PB) are still a matter of active research concerning itself with unsolved structural problems, their mixed-valence nature and their uses as important pigments, semipermeable membranes, or, in particular, PB-modified electrodes.^{7,225–228} These new metal cyanide films have been considered for various applications in electro-

chemistry (e.g. as electrochromic, electrocatalytic, and battery materials for energy storage), electrooptics, and electronics.⁶ Furthermore, interest in the ion exchange properties of polynuclear transition metal hexacyanides which was aroused by highly selective absorptions, e.g. of ¹³⁷Cs from fission product waste solutions,²²⁹ has recently been renewed in the context of *organometal-modified* Prussian Blue analogues such as 78.^{230,231} In a remarkable series of papers, Fischer et al. showed these *non-cubic* polymeric species to be made up of distorted M^B(CNSn)₆ octahedra and heavily bent [–M^BCNSn(Me₃)NC–] chains—“having missed the structure of a Super Prussian Blue”²³⁰—and to provide a zeolite-like host lattice which is particularly well suited for the reception and exchange of organic and organometallic cations eventually with formation of novel charge-transfer ion pairs.^{232,233a} Neutral molecules (“guests of guests”) from water to sugar are incorporated by [(Me₃Sn)₄Fe(CN)₆]_∞ with its “loose” SnMe₃⁺ ion.^{233b} Even chemical reactions such as spontaneous oxidation or in situ polymerization of pyrrole can occur in the channels to give “cation intercalates” [A_x(Me₃Sn)₃Fe^{II}_xFe^{III}_{1-x}(CN)₆]_∞ (1 ≥ x > 0) which are of interest as electronic (A⁺ = [1/n(C₄H₅N)_n]⁺) or potential ionic conductors (A⁺ = FeCp₂⁺, 1/nMⁿ⁺, NR₄⁺).²³⁴



79 (M = Si^{IV}, Cr^{III}; M' = Cr⁰, W⁰)



81 [Mn] = MnCp(CO)₂; [Pd] = Pd(CO)

Exhibiting exactly the same ratio (1:2) of linear to heavily bent M^AN≡C^BC≡N^A curvatures, the novel homoleptic hepta- to pentanuclear “octahedro octahedra” and “octahedro tetrahedra” supercomplexes, e.g. 79, represent a true link between the above PB and organotin-modified coordination polymers on the one side and the hundreds of oligonuclear [e.g. (Ph₃SnCl)₂(μ-NC)₂Fe(CN)₂(DMSO)₂]₂,²³⁵ [Pd₃(μ-CN)(dppe)₃]₃⁺,²³⁶ (C₆F₅)₂Pt[(μ-NC)Pd(C₆F₅)(PPh₃)₂]₂,²³⁷ [Au(CN)₂R]₄ (Figure 8),²³⁸ [Au{(μ-CN)RhCl₂-

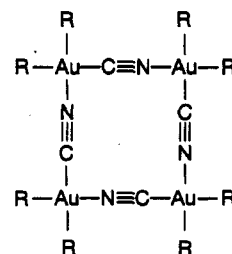


Figure 8. Structure of Au^{III}(CN)₂R₂ (R = Me, Et, Prⁿ). (The cyano groups are presumably disordered in some of the molecules.)

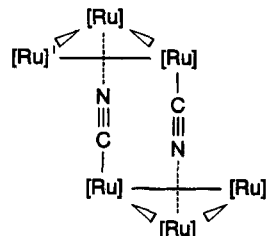
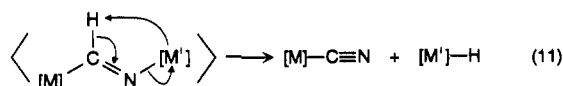
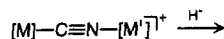
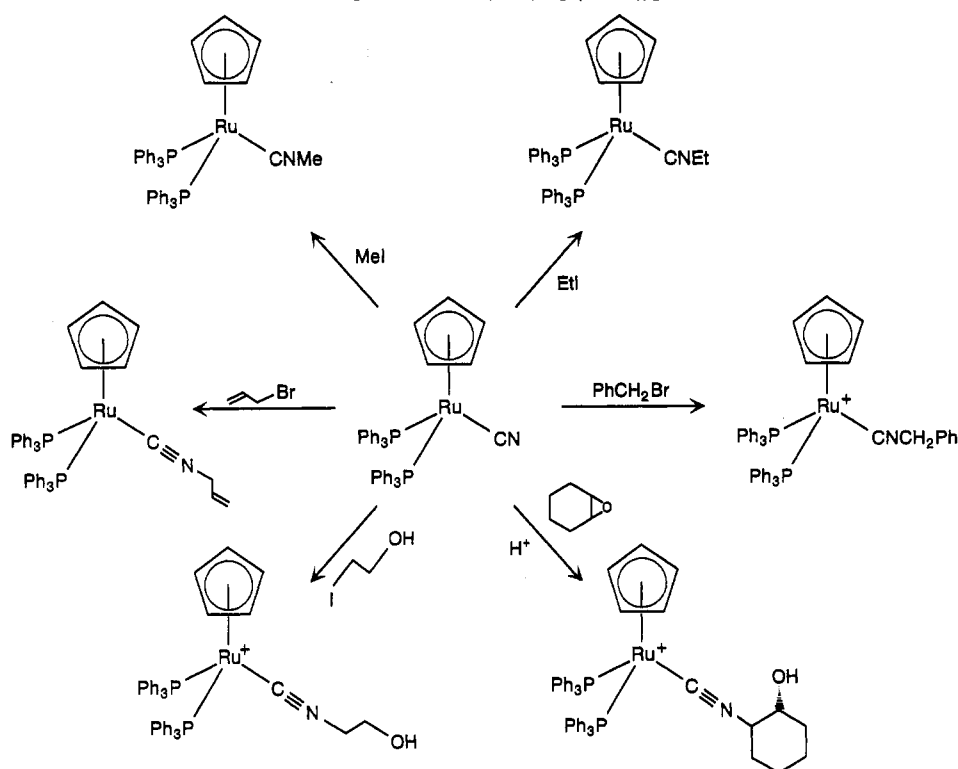


Figure 9. Dicyano-bridged metal skeleton of the cluster [Ru₆(μ-CN)₂(CO)₂₀]₂.¹⁶⁰

(PMe₂Ph)₃]₂²³⁹ down to dinuclear σ,σ-(C,N)-CN-bridged species [e.g. [Cr₂(μ-CN)(CO)₁₀]⁺, [Fe₂(μ-CN)(CO)₈]⁺,¹⁵⁶ [(NC)₅Fe(μ-CN)Cb] (Cb = cobaltamin),²⁴⁰ [(PhMe₂P)₃Cl₂M(μ-CN)M'(Cl₂(PMe₂Ph)₃)ClO₄ (M, M' = Rh or Ir),²⁴¹ [MeHgCNHgMe]⁺ (first “cyanonium complex”),²⁴² further examples are given in Sections II.A and C and refs 243 + 244], on the other.^{245,246} Very recently, these synthetic and structural studies have been extended to also include early transition metal derivatives of similar type, e.g. 80.²⁴⁷ Other recent and particularly exciting developments in the field of organometallic μ₂-CN-bridged oligomers concern Braunstein's topologically unique octanuclear Mn₄Pd₄ cluster 81,¹⁵⁹ Lavigne's hexanuclear ruthenium carbonyl cluster (see Figure 9) in which two parallel ruthenium triangles are linked by two linear cyano bridges,¹⁶⁰ and Shriver's *organometallic* modification of a molybdenum-chloride cluster, [Mo₆Cl₈(NCMn-Cp(CO)₂)₆]₂.²⁴⁸ Hanack's efforts for a polymeric μ-cyano(phthalocyaninato)cobalt(III) aim at a different goal, viz. electrical conductivity.²⁴⁹

A couple of diruthenium and mixed iron-ruthenium cyano-bridged cations of the type [CpL₂Ru(μ-CN)-ML'₂Cp]⁺ [M = Ru or Fe; L₂, L'₂ = (PPh₃)₂, dppe] have been synthesized and studied as models for the reduction of bridging isocarbonyl ligands which, on their part, might well be important species in processes such as the heterogeneous reductive polymerization of carbon monoxide. Hydride reduction of the model compound resulted in the breakage of the metal-N(μ-CN) bond to restore the original mononuclear cyanide together with the required hydrido complex. The mechanism proposed for this *first and only* reaction of a cyano bridge comprises initial nucleophilic attack of H[−] on the carbon atom of the cyano bridge to generate a bridging iminoformyl which then undergoes β-elimination (eq 11).²⁵⁰



Scheme III. Reactions at the Coordinated Ligand of $\text{Ru}(\text{CN})\text{Cp}(\text{PPh}_3)_2$ ¹²⁶

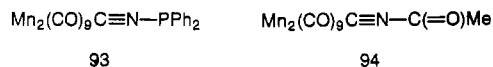
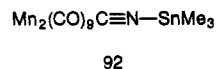
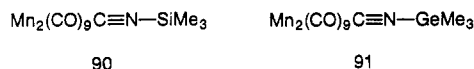
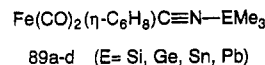
III. (Organic) Reactions at the Coordinated Ligand

A. Electrophilic Additions

1. Ionic Alkylation and Silylation to Plumbylation of Cyano Complexes

A host of alkylations of cyano complexes has accumulated since 1856 when Lieke reacted AgCN with allyliodide to produce the *first isocyanide* which thus, notably, was a *coordinated* one.²⁰³ A very readable and stimulating presentation of this early work until mid-1960 is found in Malatesta and Bonati's book on "isonitrile complexes" of which alkylations make up a considerable portion.²⁶⁴ The names of Hoelzl and Heldt must absolutely be mentioned in this context. With the emergence of strongly electrophilic alkylating agents such as methyl fluorosulfate and the trialkyloxonium tetrafluoroborates in the late 1960s the old-established ionic alkylation experienced a further impetus.^{176b,265} (From the organic point of view, a similar initiative must have come from the work of Songstad et al. who very much improved the synthesis of alkyl isocyanides by applying onium dicyanoargentates instead of silver cyanide, i.e., allowing of homogeneous reactions in aprotic solvents.²⁶⁶) Actually, looking through the literature one gets the impression that not a single cyano complex remained unalkylated. Certainly, in most cases, alkylation to give a neutral or at least "less anionic" isocyanide complex has been an integral part of the *characterization* of cyano complexes which usually has to struggle with solubility, crystallization, and/or purification problems. The same applies to the innumerable (trisorganyl-) silylations, germylations, stannylations, and even plumbylations of "organometallic" cyano compounds carried out primarily by

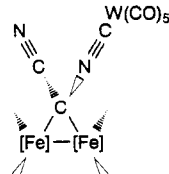
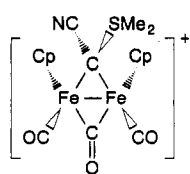
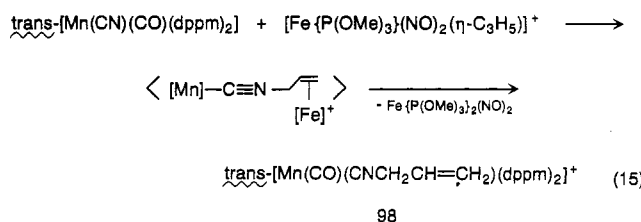
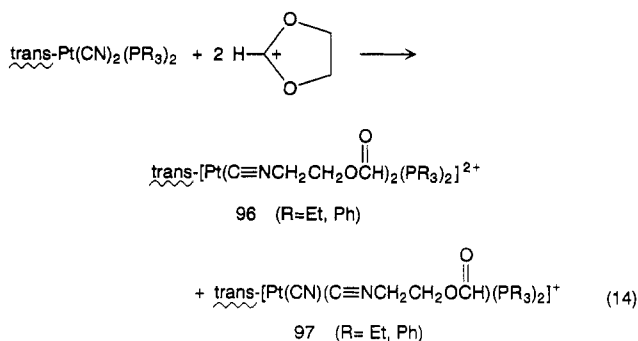
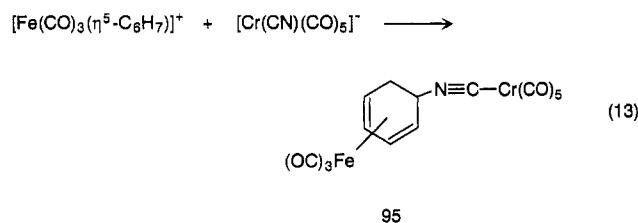
Behrens et al.¹³² Together with the "functional" isocyanides **93** and **94** (see also below), these group 14 element isocyanide derivatives of tricarbonyl(cyclohexa-1,3-diene)iron **89a-d** and decacarbonyldimanganese **90-92** constitute impressive series, after all.^{146,267}



On the other hand, relatively few of these studies have really advanced the chemistry of the metal-bonded cyanide in the sense of this article. But this can be claimed, however, by the work of Baird and Davies which is a beautiful demonstration of the nucleophilicity of the cyano ligand in electron-rich iron and ruthenium complexes (cf. Scheme III).¹²⁶ Some of the remarkable reactions in Scheme III will thus be found again in section III.D. This is also true for reactions with electrophiles of Ph_3BCN^- which has been shown by Hesse et al. to very much behave like transition metal cyano complexes (sections III.B and D).²⁶⁸

Rather sophisticated alkylating agents leading to the dinuclear cyclohexadienyl isocyanide-bridged **95** and a series of 2-isocyanoethyl formate complexes **96** and **97** have been employed by Behrens et al. and by Weigand and Beck, respectively (eqs 13 and 14).^{269,270} An unprecedented "allylic alkylation of coordinated cyano

nide" to give **98** has been reported by Connelly and co-workers. The allyl transfer from a π -allyliron complex cation to the N atom of a manganese-bound cyanide most likely proceeds via an unstable allyl isocyanide-bridged bimetallic intermediate (eq 15).²⁷¹ Perhaps the most attractive "carbocation" (**99**) ever used for cyanide alkylation, however, stems from Busetto's group; its reaction with $[\text{W}(\text{CN})(\text{CO})_5]^-$ resulted in an equally attractive trinuclear α -dimetalated "cluster isocyanide" (**100**).²⁷² "Reductive alkylation" of silver octacyanomolybdate(IV) to give the seven-coordinated $[\text{Mo}^{\text{II}}(\text{CNR})_6\text{I}]^+$ laid the foundation to a piece of modern organometallic chemistry, viz. CC coupling of coordinated adjacent isocyanide (and other C_1) ligands.^{273,274} Mention should further be made of the possibility to generate chiral metal centers by cyanide alkylation, e.g. $[\text{Co}(\text{CN})\text{Cp}(\text{CNEt})(\text{CNMe})]\text{I}$ or $[\text{FeCp}(\text{CO})(\text{CNR})(\text{CNR}')]\text{I}$, and the observation of configurationally nonlabile diastereomers in the latter case when R' equals CHMePh .^{119a,275}



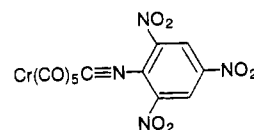
Very early attempts to synthesize alkyl isocyanide iron complexes from complex cyanide acids and primary alcohols had failed;²⁷⁶ "Buff's ferrocyanathyl" has recently been shown to be only a first step on the way to ethyl isocyanide, viz. a hexakis(hydrogen isocyanide) complex which binds to six molecules of alcohol through six strong H bridges (cf. section II.A).⁶⁵ Much later,

the synthesis was accomplished by extended heating of the components in an autoclave.²⁷⁷ Now, Weigand and Beck made use of the Mitsunobu reagent ($\text{PPh}_3/\text{diethyl azodicarboxylate}$) for a mild and efficient esterification with methanol and ethanol of the hydrogen isocyanide complexes $\text{Fe}(\text{CN})_2(\text{CNH})_4 \cdot 4\text{Et}_2\text{O}$ and $\text{Fe}(\text{CN})_2(\text{bipy})(\text{CNH})_2 \cdot 2\text{H}_2\text{O}$ to give *cis/trans*- $\text{Fe}(\text{CN})_2(\text{CNR})_4$ ($\text{R} = \text{Me, Et}$) and $\text{Fe}(\text{CN})_2(\text{bipy})(\text{CNR})_2 \cdot 2\text{H}_2\text{O}$ ($\text{R} = \text{Me, Et}$), respectively, thereby bringing an old matter to a close.²⁷⁸

2. Arylations, Acylations, and Iminoacylations

Arylation of cyano complexes to give aryl isocyanides has never developed into a preparative method, much in contrast to the many *cyanations* of haloarenes and -alkenes or even the "venerable Sandmeyer" for which transition metal (organometallic) cyanides are unre-nounceable prerequisites (cf., e.g. section II.B). While in most of these processes the essential steps are considered to be radical in nature, the conversion of $\text{IPh}_2^+[\text{Co}(\text{CN})_2(\text{dmgH})_2]^-$ (**101**) to $\text{Co}(\text{CN})(\text{dmgH})_2\text{L}$ ($\text{L} = \text{base}$, e.g. pyridine) has been discussed in terms of a *nucleophilic* attack of the CN lone pair at the *ipso*-carbon of the diphenyliodonium ion leading to the formation of iodobenzene and, ultimately, free phenyl isocyanide. Interestingly, solid-state decomposition of **101** resulted in phenylation of the dmgH ligand instead of CN.²⁷⁹ One notes the close similarity of **101** with the arene diazonium/cyanometalate systems which are known to readily generate primary (Ar^\cdot , $\text{L}_n\text{MCN}^\cdot$) and secondary radicals (derived from the solvent), though (cf. section III.B). Likewise, on irradiation into the ion pair charge-transfer band of the diphenyliodonium salt of octacyanomolybdate(IV), a "second-sphere photo-oxidation" with formation of $[\text{Mo}(\text{CN})_8]^{3-}$ and possibly some radical species, however, no CN arylation has been observed.^{280,281}

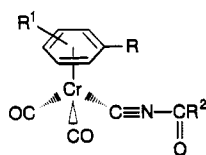
Undoubtedly an *ionic* arylation of $[\text{Cr}(\text{CN})(\text{CO})_5]^-$ to give **102** has been achieved with picryl chloride, on the other hand.²⁸²



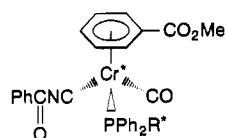
Definitely more interest has been shown in *acylations* of cyano complexes and *acyl isocyanides* as ligands, which according to ab initio LCAO-MO calculations carried out by Saillard et al. using a simple ζ basis are better σ -donors and better π -acceptors than CO, i.e. occupy an intermediate position between CO and CS.²⁸³ The first acyl isocyanide complexes, $\text{Cr}(\text{CO})_5\text{-C}\equiv\text{NC}(=\text{O})\text{R}$ ($\text{R} = \text{Ph, } o\text{-Tol, Pr}^i, \text{Cy, H}_2\text{C}=\text{CMe-}$, etc.) (**103**), have been mentioned in the patent literature, and their use in metal plating or as acylating agents was speculated.²⁸⁴ Subsequent studies confirmed the nature of **103** as activated carboxylic acid derivatives with a potential even for electrophilic acylations of aromatic compounds.^{49,285,286}

In a series of papers, Simonneaux, Jaouen, and others deal with acyl, carbamoyl, alkoxycarbonyl, and alkyl-

thiocarbonyl isocyanide derivatives of arenechromium tricarbonyl (**104a-d**) (including $\text{MnCp}(\text{CO})_2\text{CNC}(=\text{O})\text{Ph}$ and $\text{Mn}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2\text{CNC}(=\text{O})\text{Ph}$)^{128,287,288} of which several type **104a** complexes were subjected to substitution reactions both of the arene ring with CO under pressure (furnishing a new synthetic route to $\text{Cr}(\text{CO})_5\text{CNC}(=\text{O})\text{R}$ complexes)²⁸⁸ and, photochemically, of CO by phosphites or phosphines to give new chiral arene chromium(0) complexes. The exceedingly strong $\text{Cr}-\text{CNC}(=\text{O})\text{R}$ bond and the strong labilizing effect of $\text{CNC}(=\text{O})\text{R}$ on the other ligands reflected by this chemistry prompted further work on the effectiveness of the new "key ligand" $\text{CNC}(=\text{O})\text{R}$ in catalytic hydrogenations; moreover, with the successful preparation and separation of two basically different pairs of optically active configurationally ("enantiomerically") stable diastereoisomers, **105** and **106**, the possibility of asymmetric catalyses under mild conditions appears near at hand.^{127,289,290}

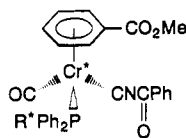


104a-d ($\text{R}^2 = \text{aryl, NMe}_2, \text{OEt, SEt}$)

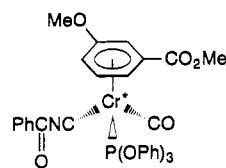


105a

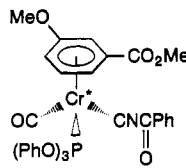
($\text{R}^* = \text{neomenthane}$)



105b



106a



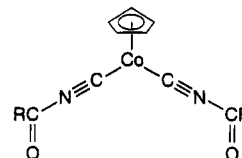
106b

One representative of each of the two extended series of acyl isocyanide complexes, $\text{Cr}(\text{CO})_5\text{CNC}(=\text{O})\text{Ph}$ and $\text{Cr}(\eta\text{-C}_6\text{H}_5\text{CO}_2\text{Me})(\text{CO})_2\text{CNC}(=\text{O})\text{Ph}$, as well as the bis(acyl isocyanide)cobalt complex **107** ($\text{R} = \text{Ph}$) have been studied by X-ray and found to essentially meet the stereochemical expectations, although no explanation was given for the observed considerable deviations of the $\text{C}\equiv\text{N}-\text{C}$ angles ($164(1)$ to $173.9(3)^\circ$) from linearity.^{289,291,292}

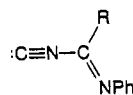
In two recent "bio-organometallic" studies, a completely different approach to acyl isocyanide and bis(acyl isocyanide) complexes was chosen, viz. introduction into coordinatively unsaturated porphyriniron systems of the free functional isocyanide which served as a particularly sensitive probe for modifications on the periphery of the porphyrin ring ("cis effect").^{293,294} Free acyl isocyanides had already been prepared by Höfle and Lange via the classical AgCN method.^{295,296} Synthesis of the more stable free *N*-imidoyl (iminoacyl) isocyanide **108** worked on the same simple principle.²⁹⁷ Earlier, action of benzoyl bromide on AgCN in acetone

had given rise to *O*-acylated isocyano hydrines (α -acyloxy isocyanides) **109** (cf. section III.C).²⁹⁸

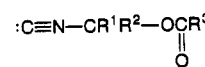
Cyclovoltammetric studies and first reactions have been carried out on the cobalt species **107** which had been obtained either by displacement of both CO groups from $\text{CoCp}(\text{CO})_2$ by $\text{CNC}(=\text{O})\text{R}$ or, in low yields, from $[\text{Co}(\text{CN})\text{Cp}(\text{CO})]^-$ (cf. section II.B) and acyl chlorides lacking α -hydrogens.^{102,292} Although definitive results are lacking, most findings are consistent with benzoyl isocyanide being a stronger π -acceptor than the saturated acyl isocyanides and CO.²⁹²



107 ($\text{R} = \text{Bu}^t, 1\text{-adamantyl, Ph}$)



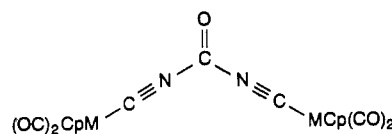
108 ($\text{R} = \text{Ph, Bu}^t$)



109

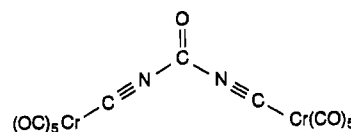
(e.g. $\text{R}^1 = \text{Ph, R}^2 = \text{R}^3 = \text{Me}$)

Three complexes **110-112** containing the carbonyl diisocyanide bridge have been reported. While **110** and **111** resulted from simply reacting the parent cyano complexes with phosgene 2:1,²⁹⁹ it was a much less straightforward process, viz. the conductance *in air* of the "radical alkylation" of $[\text{Cr}(\text{CN})(\text{CO})_5]^-$ in chloroform, that first led to the dichromium complex **112**.³⁰⁰ However, synthesis from $[\text{Cr}(\text{CN})(\text{CO})_5]^-$ and phosgene is a strongly preferable alternative.⁴⁵

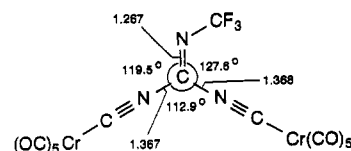


110 $\text{M} = \text{Mn}$

111 $\text{M} = \text{Re}$



112



113

Unfortunately, little is known about the bonding in these highly unsaturated and certainly highly electrophilic systems, and nothing is known about their chemistry. Behrens et al. ventured an IR assignment

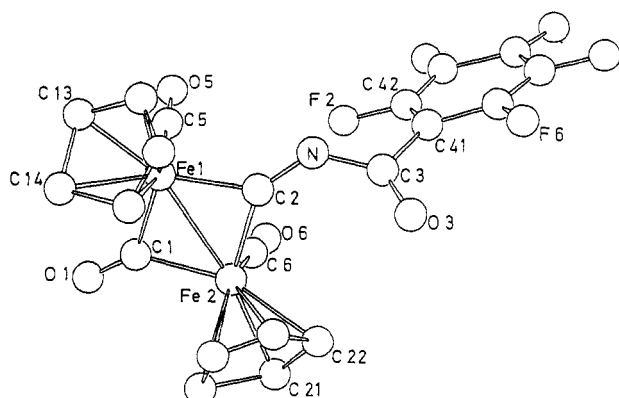


Figure 12. ORTEP drawing of 114f.

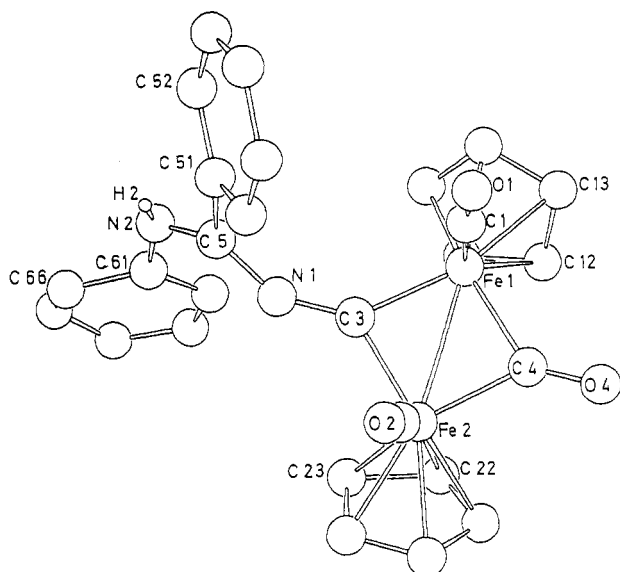


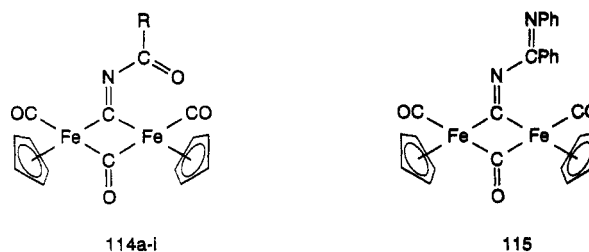
Figure 13. Structure of the complex cation of 116.

from the band shifts in the high-frequency region on addition of AlCl_3 to a solution of 110. Three bands (2017 s, 1939 vs, and 1770 vs cm^{-1}) moved to higher wavenumbers (2036 s, 1981 vs, and 1891 s cm^{-1}) and thus were assigned to the $\nu(\text{CN})$ and $\nu(\text{CO})$ species, while, expectedly, the stretching vibration of the complexed keto group went down (from 1687 s to 1650 s cm^{-1}).²⁹⁹ Of a related complex 113, product of the reaction between $[\text{Cr}(\text{CN})(\text{CO})_5]^-$ and the isocyanide dichloride $\text{CF}_3\text{N}=\text{CCl}_2$, the molecular structure was established by an X-ray analysis.³⁰¹

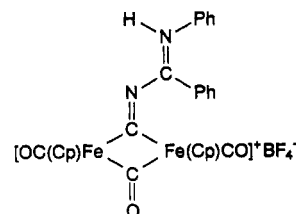
Fehlhammer et al. very recently reported on di(cyclopentadienyl)tricarbonyldiiron complexes with various acyl, aroyl, carbamoyl, and imido isocyanide bridging ligands, 114a-i and 115, which had been synthesized by acylation (aroylation, etc.) with the respective acid chlorides of the terminal cyano ligand in $\text{Na}[\text{Fe}_2(\text{CN})\text{Cp}_2(\text{CO})_3]$ (cf. sections II.A and B).³⁰² Analogous compounds with $\text{CNC}(=\text{O})\text{SR}$ bridges surprisingly form by insertion of NCO - in the $\text{C}(\text{carbyne})-\text{S}$ bond of corresponding (μ -alkylthiocarbyne)diiron systems.³⁰³ From ^{13}C labeling of the isocyanide carbon atom in 114e, the $\nu(\text{CN})$ motion was assigned to the strong band between 1600 and 1650 cm^{-1} , and the ^{13}C NMR resonance of $\mu\text{-CNC}(=\text{O})\text{R}$ was detected around δ 264 \pm 3, i.e. at slightly higher fields as compared with $\mu\text{-CO}$. An X-ray structure analysis of 114f revealed a cis configuration of the complex, a 163.7° puckering of the central $\text{Fe}_2(\mu\text{-C})_2$ rhomboid, short [1.892(5), 1.911(5)

Å] $\text{Fe}-\mu\text{-C}$ distances to the acyl isocyanide ligand and a 132° bend at the isocyano nitrogen. The most salient structural feature, however, is the helical twist of altogether 112° of the main atomic sequence $\text{Fe}^2\text{-C}2\text{-N-C}3\text{-O}$ or $\text{Fe}2\text{-C}2\text{-N-C}3\text{-C}41\text{-C}42$, respectively, of the molecule 114f (Figure 12).³⁰²

Very interestingly, a practically identical value (111°) for the overall torsion angle along $\text{Fe}1\text{-C}3\text{-N}1\text{-C}5\text{-C}51\text{-C}56$ has been measured in 116 (Figure 13), product of the protonation of 115 which in the same way as alkylation exclusively occurred at the imino nitrogen. (In contrast, the acyl isocyanide bridged diiron complexes 114 are protonated at the isocyano nitrogen to give cationic μ -aminocarbyne complexes.)³⁰⁴

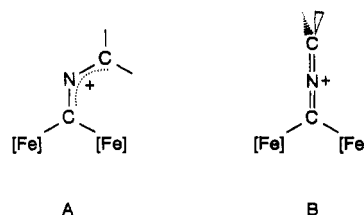


	R		R		R
114a	Et	114d	4-MeOC ₆ H ₄	114g	CCl ₃
114b	CH=CH ₂	114e	4-O ₂ NC ₆ H ₄	114h	CF ₃
114c	Ph	114f	C ₆ F ₅	114i	NMe ₂



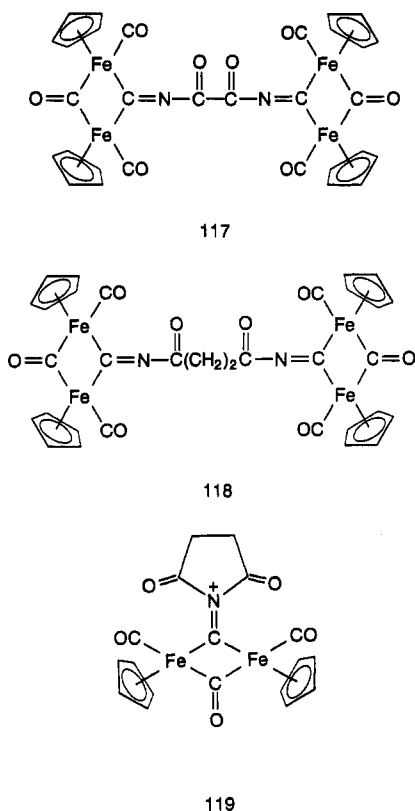
116

Both stereochemistries concurrently support a description of the bonding in the bridging region as hybrid of μ -2-azaallylidene- (A) and μ -2-azaallenylidene-type (B) resonance structures. Moreover, a striking similarity between organometallic, i.e. mono- to tetrametalated (section III.E) heterocumulenes and heterodienes on the one side, and the purely organic systems on the other has been stated and considered a particularly important point.



With the dicarboxylic acid dichlorides succinyl dichloride and oxalyl chloride, $\text{Na}[\text{Fe}_2(\text{CN})\text{Cp}_2(\text{CO})_3]$ reacted in a 1:2 fashion to give the tetranuclear species 117 and 118, i.e. no diacylation of the cyano ligand took place despite the sterically (and entropically) favorable situation for the formation of 119 in the reaction with $\text{ClC}(=\text{O})\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{Cl}$. Later, a minor byproduct

was identified which could have formed via 119, however.³⁰⁵ This, and in particular the reaction with phthaloyl dichloride, opened up a fascinating chemistry, reaching far beyond simple cyanide acylation, which is dealt with in a separate paragraph (section III.E).



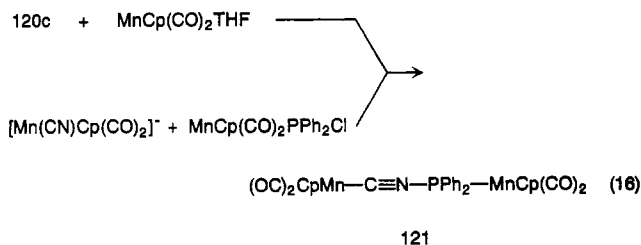
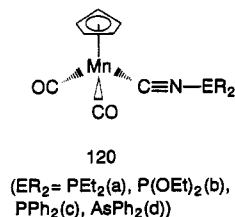
3. "Functional" Isocyanides

This section certainly overlaps the two preceding ones and the following. Not only that there is no unequivocal definition as to the term "functional" (e.g., the SnMe_3 group may or may not be regarded as functional), it is more for the sake of clarity that this part is separated from say the acyl isocyanides (although these are clearly functional).

The field of functional isocyanides in a narrower sense, amazingly, is widely unexplored, at least, as far as syntheses from cyano complexes are concerned. The first metal-stabilized P- (and As-) isocyanides 93 and 120a-d were independently and simultaneously prepared by the groups of Behrens and Höfler in 1979.^{146,306} The moderately light-sensitive compounds which have been characterized by the usual spectroscopic methods (IR, ^1H and ^{31}P NMR, mass spectroscopy) showed no tendency to rearrange to P-bonded isomers. The "functionality" of the P-isocyanide was demonstrated by Höfler through its coordination onto a second manganese complex fragment to give an isocyanophosphine-bridged dimanganese species 121 for which an alternative synthetic route was devised in addition (eq 16). Isocyanodimethylarsine stabilized by the complex fragments $\text{MnCp}(\text{CO})_2$ and $\text{ReCp}(\text{CO})_2$ has also been reported.²⁹⁹

The existence of related N-isocyanides which, however, are not accessible via electrophilic additions to cyano complexes is noted.³⁰⁷

There is a report which presents quite convincing experimental evidence for the existence of the thioful-



minate ligand as a bridge in polymeric material which has been obtained by reacting potassium hexacyanoferrate(III) with molten sulfur at 200 °C. Clearly, more work is needed to fully characterize this material and to get hold of discrete complexes of this simplest S-isocyanide which obviously is sufficiently stable.³⁰⁸

Less spectacular yet well-defined S-isocyanides, the organosulfonyl isocyanide chromium complexes 122 derived from cyanide and RSO_2Cl , come again from Höfler's laboratory.³⁰⁹ The pronounced π -acceptor ability of the new ligand shows up in unusually high $\nu(\text{CN})$ —[E] modes ($\approx 1980 \text{ cm}^{-1}$). 122a had been synthesized before by dechlorination ("three component oxidative addition") of $\text{PhSO}_2\text{N}=\text{CCl}_2$ with $\text{Na}_2[\text{Cr}(\text{CO})_5]$.³¹⁰ By a similar route, i.e. debromination of the appropriate isocyanide dibromide with methyl-lithium sulfur pentafluoride isocyanide, SF_5NC , has recently been obtained.³¹¹

Although "only a C-isocyanide", CNCN (isocyanogen, cyanoisocyanide) is of topical interest to synthetic chemists, spectroscopists, and theoreticians, not least for its possible role in interstellar chemistry.³¹²⁻³¹⁴ In the form of pentacarbonylchromium complex 123 it is readily available and easy to handle,³¹⁵ much in contrast to free CNCN now generated by flash vacuum pyrolysis of norbornadienone azine or, better, N-cyano-2,3-diphenylcyclopropaneimine.^{312a,316} [Also note, that the third isomer, viz. the N-isocyanide CNNC (diisocyanogen) has just been generated by a microwave discharge in acetylene/ N_2 and studied in a matrix at 12 K.³¹⁷] The stereochemistry of 123 as revealed by an X-ray structure analysis (Figure 14) reflects the unique electronic properties of this ligand which is a much better π -acceptor than CO.²⁸³ That CNCN is in fact an extremely electron-deficient moiety is further borne out by the IR pattern (1992 s [$\nu(\text{CO})$ —E], 1952 s, br cm^{-1} [$\nu(\text{NC})$]?), a strikingly low isocyano ^{13}C resonance ($\delta 200.0$ [CrCN]), and a high chemical reactivity.^{315,318,319}

124, a formal trimer of 123, resulted from the reaction of $[\text{Cr}(\text{CN})(\text{CO})_5]^-$ with cyanuric chloride; however, no conversion $123 \rightleftharpoons 124$ was possible in either direction.³¹⁵

Neutral "B-isocyanides" (125–128) with tri- and tetracoordinated boron atoms have been derived from bromo- or chloroboranes (BXR_2) and $\text{BCl}_2(\text{OMe})\cdot\text{NMe}_3$ by $\text{X}^-/[\text{Cr}(\text{CN})(\text{CO})_5]^-$ exchange at low temperatures. Both, their mode of preparation and their functionality

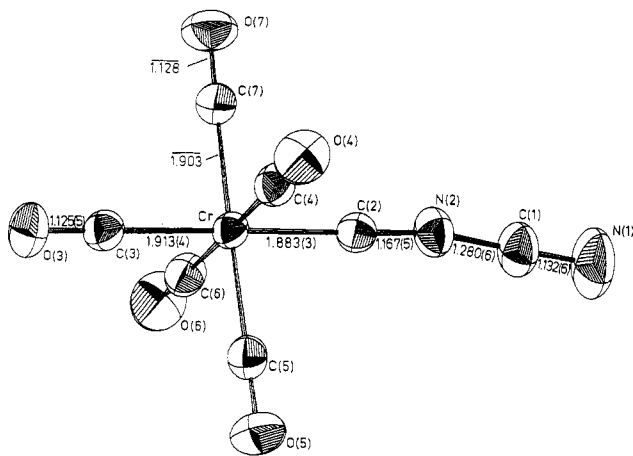
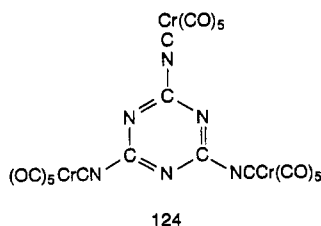
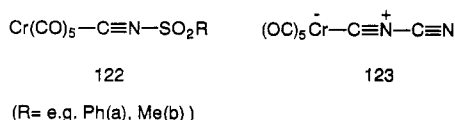
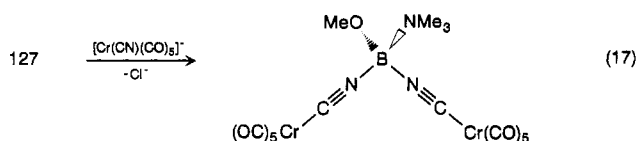
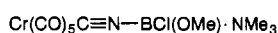
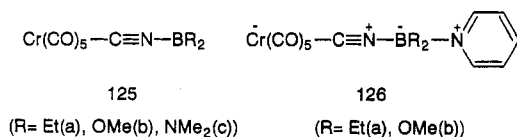


Figure 14. The structure of $\text{Cr(CO)}_5\text{CNCN}$ and important molecular parameters. Average bond lengths are given for the cis Cr-C and C-O groups.³¹⁵



as expressed by the formation of adducts (125a,b \rightarrow 126a,b) and bridges (eq 17) justify their discussion in this context while simple (anionic) cyanide-borane adducts are treated in sections II.C and III.A.4. From CO force constant calculations and Graham's σ - and π -bonding parameters it has been deduced that the isocyanoboranes in 125–128, perhaps unexpectedly, are weaker σ -donors and π -acceptors than CNBu^t .³²⁰ Earlier, free trimethylamine-isocyanoborane, $\text{C}\equiv\text{N—BH}_2\cdot\text{NMe}_3$, had been obtained from the action of an 8-fold excess $\text{BH}_2\text{I}\cdot\text{NMe}_3$ on $\text{K}[\text{Ag}(\text{CN})_2]$ and was subsequently introduced into AgCN and $\text{MnBr}(\text{CO})_5$.³²¹

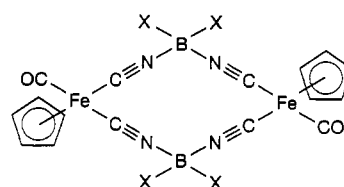
Tricoordinate boron also appears to exist in the isocyanoborane species $\text{Fe(CO)}_3\{\text{CNB}(\text{NMe}_2)_2\}_2$ and $\text{Ni(CO)}_3\text{CNB}(\text{NMe}_2)_2$ prepared from the metal carbynls and the cyanoborane $\text{B(CN)(NMe}_2)_2$.³²²



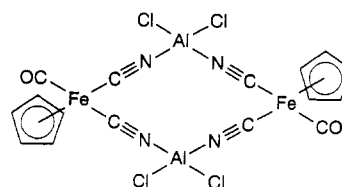
128

4. Lewis Acid Adducts

From the reaction of $\text{K}[\text{Fe}(\text{CN})_2\text{Cp}(\text{CO})]$ with the boranes BX_3 ($\text{X} = \text{F, Cl, Br, H, Ph}$), Emri et al. had obtained both, simple addition compounds such as $\text{K}[\text{Fe}(\text{C}\equiv\text{NBX}_3)_2\text{Cp}(\text{CO})]$, where $\text{X} = \text{Ph}$ or H , and complexes with a stoichiometry of only *one* BX_2 group per *two* CN ligands. From molecular weight determination and mass spectrometry, dimeric structures (129) with the novel diisocyanodifluoro-, diisocyanodibromo-, and diisocyanodiphenylborate bridging ligands were assumed for the latter products of which 129a and 129b showed an exceptional resistance to oxidizing agents, mineral acids, and bases. A much less stable “Al-isocyanide” presumably having the same 12-membered ring structure (130) has been mentioned.³²³ Also,



129 ($\text{X} = \text{F(a), Br(b), Ph(c)}$)



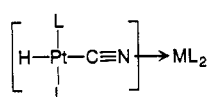
130

$\text{Fe(CN)}_2(\text{phen})_2$ and Fe(CN)Cp(CO)_2 have been studied in the AlCl_3/n -butylpyridinium chloride molten salt system by IR and UV/vis spectroscopies, and adducts such as $[\text{Fe}]\text{C}\equiv\text{NAlCl}_3$ and $[\text{Fe}]\text{C}\equiv\text{NAl}_2\text{Cl}_6$ have tentatively been formulated.³²⁴

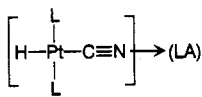
Though isocyanoborane or diisocyanoborates may occasionally form in reactions of anionic transition metal cyano complexes with BX_3 , the vast majority of products is clearly of the type of simple addition compounds. Most of these early homoleptic $[\text{M}(\text{C}\equiv\text{NBF}_3)_n]^{z-n}$, $\text{M} = \text{Ni}^{\text{II}}, \text{Fe}^{\text{II}}, \text{Mo}^{\text{IV}}$; $n = 4, 6, 8$ and heteroleptic [e.g. $\text{Fe}(\text{C}\equiv\text{NBX}_3)_2(\text{phen})_2$] adducts are from the laboratory of Shriver and have been summed up in a review entitled “The Ambident Nature of Cyanide”.^{3,325} In the infrared, a substantial increase of the CN stretching frequency by 50 to over 100 cm^{-1} is observed upon addition of BF_3 and generally taken as evidence for CN bridging to have occurred.³²⁶ In contrast, $\nu(\text{MC})$ is relatively insensitive to adduct formation as indicated by a shift of the T_{1u} FeC stretch from 417 cm^{-1} in $\text{K}_4[\text{Fe}(\text{CN})_6]$ to only 422 cm^{-1} in $\text{K}_4[\text{Fe}(\text{CNBF}_3)_6]$.³²⁷ The change in the antisymmetric CO stretching frequency, $\Delta\nu_{\text{as}}(\text{CO})$, which occurred upon coordination of a Lewis acid to Fe(CN)Cp(CO)_2 had been used as a convenient probe for the relative electron pair acceptor strength of the acid, which increases according to $\text{BH}_3 < \text{BF}_3 < \text{BCl}_3 \approx \text{BBr}_3, \text{AlCl}_3 < \text{GaCl}_3 < \text{BCl}_3$ and $\text{BMe}_3 \approx \text{GaMe}_3 < \text{AlMe}_3$.³²⁸ A similar order had been obtained from the observed changes in the charge transfer spectra of $\text{Fe(CN)}_2(\text{phen})_2$ and $[\text{Fe(CN)}_2(\text{phen})_2]\text{PF}_6$ upon adduct formation, and the effects have been interpreted

in terms of a decrease in the metal–ligand σ -bonding and an increase in π -bonding.³²⁹ Relative Lewis acidities decreasing in the order $\text{AlCl}_3 > \text{BAr}_3 > \text{BR}_3 \approx \text{CoCl}_2 > \text{AlAr}_3 > \text{ZnCl}_2 > \text{B(OAr)}_3 > \text{AlR}_3 > \text{AlR}_2(\text{OR})$ have been deduced from variations in the coupling constants, $^1J(\text{Pt}–\text{H})$, with the Lewis acid of the hydridoplatinum complexes 131.³³⁰

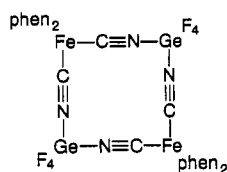
Group 14 Lewis acid adducts to cyano complexes have also been studied. Here, in particular, the reaction of GeF_4 with $\text{Fe}(\text{CN})_2(\text{phen})_2$ led to a surprising variety of compounds, the 1:1 adduct of which was formulated as a dimer (132).³³¹



131a (M = Zn, Co, Ni)

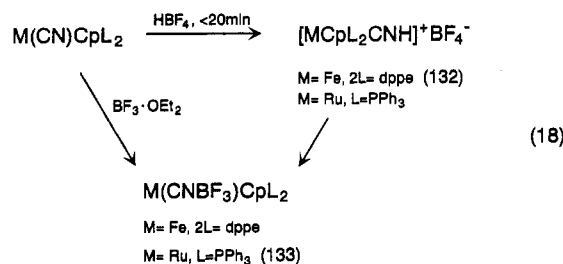


131b

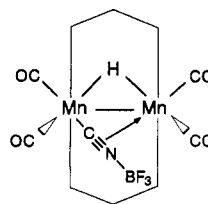


132

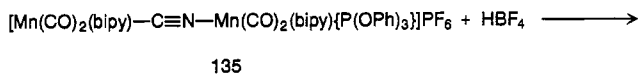
Occasionally, L_nMCNBF_3 complexes have unexpectedly been isolated on attempted protonations of cyano complexes with aqueous [e.g. $\text{Mn}(\text{CNBF}_3)(\text{CO})_2(\eta\text{-C}_6\text{H}_3\text{Me}_3)$]³² or etheral HBF_4 [e.g. *cis/trans*- $\text{Mn}(\text{CNBF}_3)(\text{CO})_2\text{bipy}\{\text{P}(\text{OPh})_3\}$, $\text{Fe}(\text{CNBF}_3)\text{Cp}(\text{dppe})$].^{61,332} However, the desired hydrogen isocyanide complexes actually appear as primary products and can be obtained by a quick workup (cf. 132, eq 18 and ref 40). The first crystal structure of a CNBF_3 complex, 133, has been determined by Beck et al. who in addition presented valuable IR ($1140\text{--}1086\text{ cm}^{-1}$ [$\nu_{\text{as}}(^{10/11}\text{BF}_3) + \nu(^{10/11}\text{BN})$], $897\text{--}861\text{ cm}^{-1}$ [$\nu_{\text{s}}(^{10/11}\text{BF}_3)$]) and NMR data (^{11}B) characteristic for coordinated BF_3 .⁴⁰



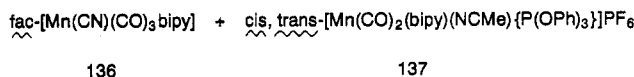
Two reports are concerned with the action of BF_3 (HFB_4) on cyanide-bridged dimanganese systems. While in 134 the unique $\mu\text{-}\eta^1, \eta^2\text{-CN}$ structure was fully retained—the only effect of BF_3 addition being some lowering of the rate of the “windshield-wiper” oscillation of the ligand between the two manganese atoms⁴²—the “normal” (yet severely bent, cf. section II.D) cyano bridge in 135 was cleaved by $\text{HBF}_4 \cdot \text{OEt}_2$ /acetonitrile followed by addition of NEt_3 (eq 19). $[\text{Mn}]\text{CNH}^+\text{BF}_4^-$ (which subsequently gives $[\text{Mn}]\text{CNBF}_3$ and 136), and $[\text{Mn}]^+$ that readily coordinates MeCN to give 137 have been proposed as transient species.³³²



134



(19)



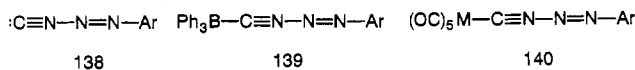
B. “Radical Alkylation” of Cyano Complexes and Secondary Reactions

This section deals with syntheses of isocyanides from cyano complexes which, in contrast to the classical ionic CN alkylation (section III.A.1), are basically radical in nature, leading to products typical of a radical reaction pattern. The functional isocyanides generated that way are absolutely unique in a sense that no other synthetic route has so far been developed nor even seems conceivable for their preparation, least of all conventional *organic* procedures which would have to manage without a protecting metal.

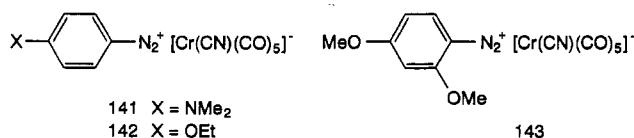
The special features of these novel functional isocyanides naturally show up in their chemistry which is particularly rich in the case of the α -halogenoalkyl derivatives. Actually, it is this kind of an “activated form of cyanide” which contributed most of the “emerging organometallic chemistry of CN”; therefore, a survey of “secondary reactions” will be given in section III.B.3.

1. Interactions between Diazonium Salts and Cyanometalates

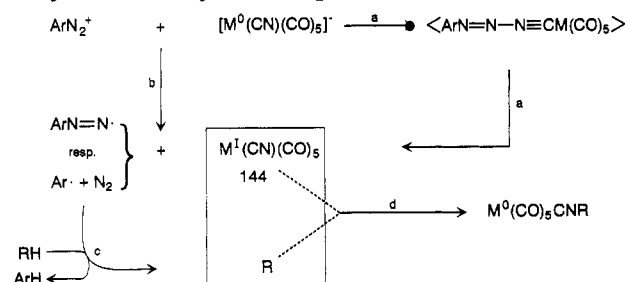
There are reports both on “free” (138) and BPh_3 -coordinated diazoisocyanides (isocyanodiazenes) (139) neither of which, however, could be confirmed.^{268,333,334} The system $\text{ArN}_2^+ / [\text{M}(\text{CN})(\text{CO})_5]^-$ (M = Cr, Mo, W), too, evades formation of covalently bound *N*-isocyanides of type 140; instead, depending on the kind of sub-



stituents at the benzene ring, either immediate decomposition with evolution of N_2 takes place even at low temperatures, or the diazonium cations and cyanometalate anions coexist in salt-like compounds (141–143) of moderate thermal stability. For the latter to



occur, electron-donating substituents are required in the diazonium component which lower both its electrophilicity and oxidation potential. Even the most

Scheme IV. Proposed Mechanism of the "Radical Alkylation" of Cyano Complexes

stable diazonium/cyanochromate combination 141, however, slowly decomposes in solution at room temperature thereby forming radical species which have been detected by ESR measurements.

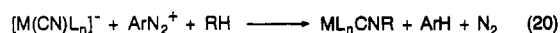
From mixtures of $\text{Na}[\text{M}(\text{CN})(\text{CO})_5]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) and the arenediazonium chlorides $[4\text{-X}\text{C}_6\text{H}_4\text{N}_2]\text{Cl}$ ($\text{X} = \text{H}, \text{Cl}, \text{Br}$) either dissolved or suspended in various media, nitrogen is spontaneously released at temperatures between -50 and -20°C . As organometallic products, pentacarbonyl isocyanide complexes have been isolated, the isocyanide side chains of which were derived from the respective solvent.^{48,335,336}

The mechanism outlined in Scheme IV is supported by various chemical and spectroscopic observations including electrochemical investigations which are in favor of a neutral $17e^-$ species $\text{Cr}^1(\text{CN})(\text{CO})_5$, having a lifetime of seconds (cf. section II.B).¹⁵⁰ In the first step, a single electron transfer (SET) takes place between the diazonium cation and the cyanometalate anion, either via a short-lived isocyanodiazene intermediate

("inner sphere", route a) or directly ("outer sphere", path b) to give a relatively stable organometallic radical (144) and a high energy aryl radical which immediately reacts with the solvent with H abstraction (c). Finally, 144 combines with the main radical of the solvent (d).^{48,335}

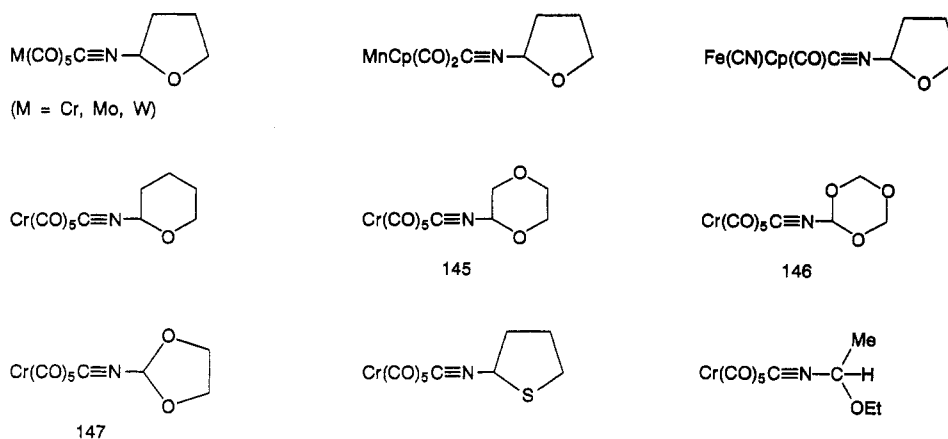
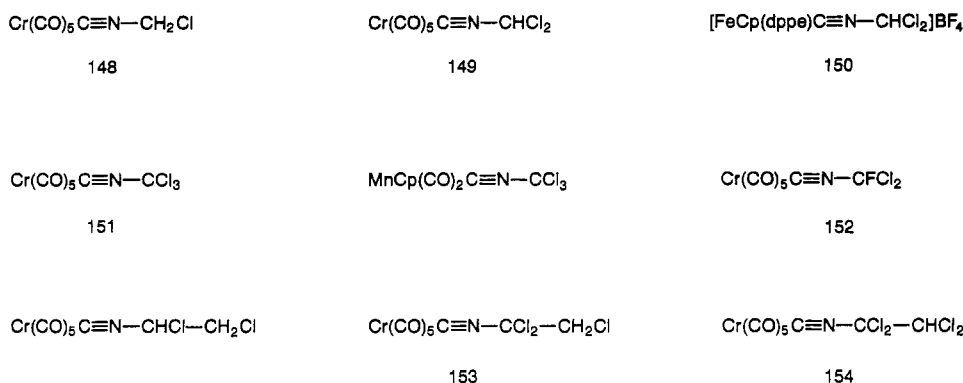
2. Syntheses of Functional Isocyanides in the System $\{\text{ArN}_2^+ / [\text{M}(\text{CN})\text{L}_n]^- / \text{Solvent}\}$

New types of α -functionalized isocyanides have been synthesized at the "protective metal" according to eq 20. Extensive variation of the solvent RH (tetrahy-

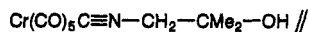


drofuran, tetrahydropyran, 1,4-dioxane, etc., or dichloromethane, chloroform, etc., respectively) together with some minor variation of the cyanometal component $[\text{M}(\text{CN})(\text{CO})_5]^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), $[\text{Mn}(\text{CN})\text{Cp}(\text{CO})_2]^-$, $[\text{Fe}(\text{CN})_2\text{Cp}(\text{CO})]^-$, $\text{Fe}(\text{CN})\text{Cp}(\text{dppe})$ gave rise to the complexes shown in the Schemes V and VI. Several of the compounds (e.g. 145 and 151–154) are obtained in surprisingly high yields, others (e.g. 146–148) only in traces due to competing side reactions such as polymerization (e.g. of 1,3-dioxolane), Meerwein reduction (of the diazonium ion by the ether), or CO capture (see below).^{48,300,335} The cationic dichloromethyl isocyanide iron complex 150 has recently been characterized by an X-ray structure analysis.³³⁷

Oxiranes, contrary to the above reaction scheme, experience ring opening with formation of β -hydroxyalkyl isocyanides, e.g. 155 or 156,³³⁵ which, however,

Scheme V. O(S)-Heterocyclic Isocyanides from "Radical Alkylation" of Cyano Complexes in Cyclic Ethers and Diethyl Ether**Scheme VI. α -Halogenoalkyl Isocyanides (via the Protodediazotization Route)**

are preferably synthesized by the ionic approach $[M(CN)(CO)_5]^-/H^+/oxirane$ (see section III.D).

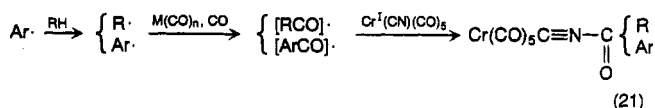


155a, b



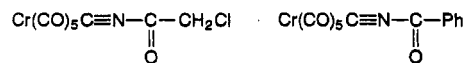
156

In less reactive and less polar solvents (CH_3Cl and CHF_2Cl), i.e. in cases where particularly short-lived radicals occur, formation by CO capture of acyl ($[Cr]CNC(=O)R$) and/or aroyl isocyanide complexes ($[Cr]CNC(=O)Ar$), e.g. 157 or 158, becomes prevalent (eq 21). (μ -Carbonyldiisocyanide)bis(pentacarbon-



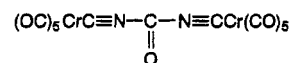
ylchromium) (159) has been identified as the main product when the radical alkylation in chloroform was conducted in the presence of dioxygen. Presumably, autoxidation of $CHCl_3$ enhanced by radical species generates phosgene which subsequently acylates two cyano complex anions; the latter reaction step has successfully been applied to directly synthesize 159 as well as a series of analogous molecules (cf. section III.A.1).³⁰⁰ In brominated or iodinated solvents, bromo- or iododediazotation is much more favorable than protodediazotation. Dibromomethane thus gave the monobromomethyl isocyanide complex 160 together with the CO-inserted products 161 and 158.

From the fully halogenated dibromodifluoromethane small amounts of 162 have been obtained. In CCl_4 , $Cr(CO)_5CNCCl_3$ (151) is formed via chlorodediazota-



157

158

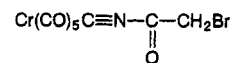


159

tion which, however, is less efficient than the route via protodediazotation in $CHCl_3$. Perfluoroalkyl iodides, finally, proved to be valuable sources of C_nF_{2n+1} radicals for the synthesis in metal complexes of the perfluoroalkyl isocyanides 163–165.³⁰⁰ (A procedure for “free” trifluoromethyl isocyanide has been worked out by Lentz.³³⁸)



160



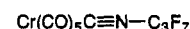
161



162



163



164

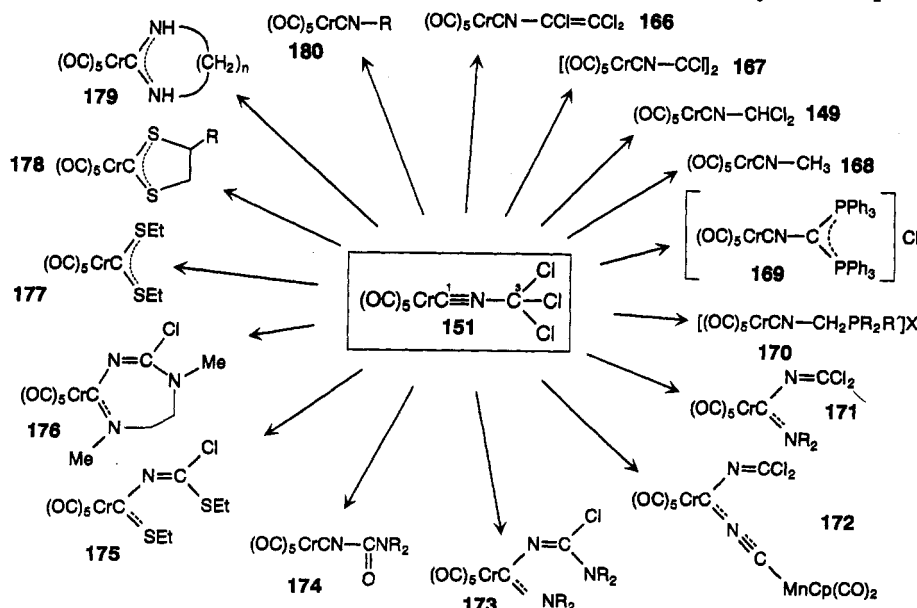


165

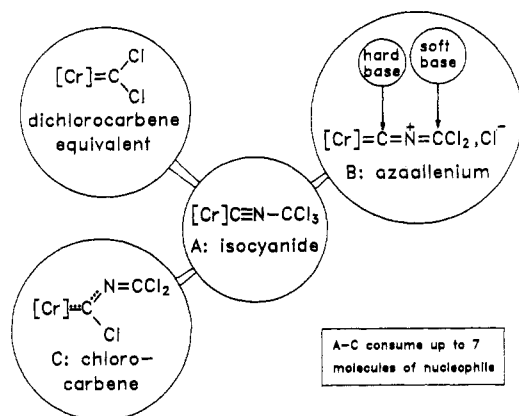
3. Selected Reactions of Coordinated α -Chloroalkyl Isocyanides

A brief survey is given primarily of the chemistry of 151, which due to the presence of two mutually reinforcing electrophilic centers, the unsaturated isocyano unit and the perchlorinated α -C atom, possesses an extremely high synthetic potential (Scheme VII). Although it is possible, in some cases, to limit the reaction to the trichloromethyl group of 151 and thereby obtain new functional isocyanides (166–170), most

Scheme VII. Products and Conditions of Selected Reactions of the “Activated Cyano Complex” 151^a

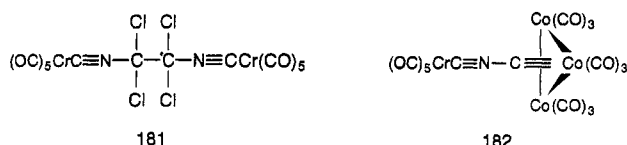


Scheme VIII. Alternative Formulae and Formulations for 151 To Rationalize the Reaction Products in Scheme VII

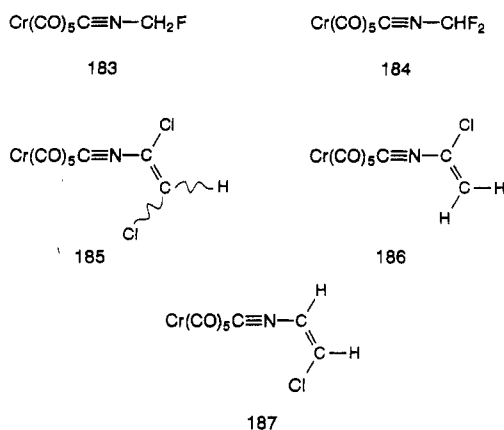


reactions occur at the two electrophilic centers (C^1 , C^3) jointly; i.e., the trichloromethyl isocyanide ligand (A) reacts as if it existed in the azaallenylium (B) or chloro(imino)carbene isomeric form (C), or even as a dichlorocarbene equivalent (Scheme VIII), affording a broad palette of carbene (171–173, 175, 177), heterocycle (176, 178, 179), and isocyanide complexes (180) (Scheme VII).³³⁹

(a) Reduction of 151 with zinc in aprotic media led to a mixture of products from which the CC-coupled chlorinated alkenyl isocyanide complexes 166 and 167 were isolated. Reductive CC coupling has also been observed upon reaction of 151 with $NaBH_4$ (to give 181 together with some 149) as well as with iron carbonyl. On the other hand, the main product of the reaction with cobalt carbonyl is the isocyanomethylidene-bridged tetranuclear cluster 182 ("permetalated methyl isocyanide").³⁴⁰ In protic solvents, the replacement of Cl by H dominates: with PPh_3 in ethanol, this process could be stopped at the stage of the dichloromethyl isocyanide complex 149 while complete reduction to methyl isocyanide (168) occurred with zinc in glacial acetic acid.

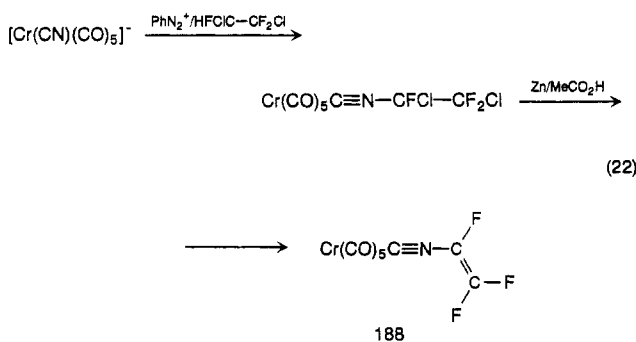


In 152, exchange of Cl for H to give 183 was achieved with tributyltin hydride; pentacarbonyl(difluoromethyl isocyanide)chromium (184), the still missing member

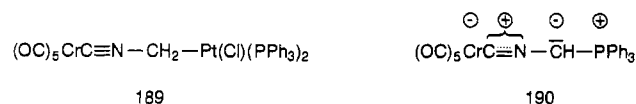


of the fluoromethyl isocyanide family, was obtained from 149 by a halogen-exchange reaction with HgF_2 as fluorinating agent.³⁴¹

Treatment with $Zn/MeCO_2H$ of the tri- and tetrachloroethyl isocyanide complexes 153 and 154, on the other hand, causes elimination of chlorine to give the chlorovinyl isocyanide complexes 185 (as a mixture of cis and trans isomers), 186 and 187.³⁴² Following an identical approach (eq 22), the fluorovinyl isocyanide complex 188 has now been prepared and subjected to flash vacuum pyrolysis at 240 °C to get hold of the first fluorinated alkenyl isocyanide $F_2C=CFNC$.³⁴³ Using the same method, Lentz et al. had generated the "interstellar molecule" ethynyl isocyanide ($C≡NC≡CH$) from 185 (154) before.³⁴⁴



The system " $Cr(CO)_5CNCCL_3/PR_3$ " turned out to be a true bonanza for versatile organometallic synthons and syntheses;³⁴⁵ thus, in addition to the organophosphorus ligands in 169 and 170, the latter of which is also accessible by a different ("metal-free") route,³⁴⁶ the long sought after monochloromethyl isocyanide 148 has recently been prepared in good yield from {151/phosphoric acid triamide/ H_2O } and converted into the first stable metal-coordinated α -metalated methyl isocyanides, e.g. 189.³⁴⁷ An even more promising synthon due to its nature as a combined isocyanide-Wittig/metallo-nitrile-ylide reagent is the α -deprotonated α -phosphino methyl isocyanide complex 190 which opens up an easy synthetic approach to both alkenyl isocyanides and diverse triphenylphosphino-substituted [3 + 2] cycloaddition products.^{346,348}



(b) N and S nucleophiles, as a rule, attack the isocyanide carbon atom and, simultaneously, cause the departure of a chloride ion from the trichloromethyl group. Examples of such products are the molecules 171 and 172 (Scheme VII), yet a whole lot more including those derived from coordinated dichloromethyl, 1,1,2-trichloroethyl, and 1-chlorovinyl isocyanide (149, 153, and 186, respectively) have meanwhile been described.^{349,350}

An X-ray structure analysis has been carried out on 172 (Figure 15). It reveals the presence of a novel isocyanocarbene bridging ligand which contains both a linear and a bent CNC unit sharing the carbene carbon atom. The cumulene-like bonding situation along the linear $C^1-N-C-Mn$ atomic sequence moreover demonstrates that the isocyanide function which is well known

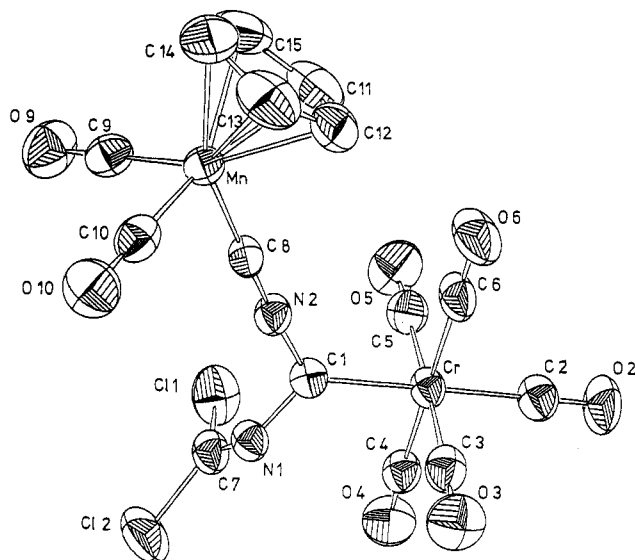
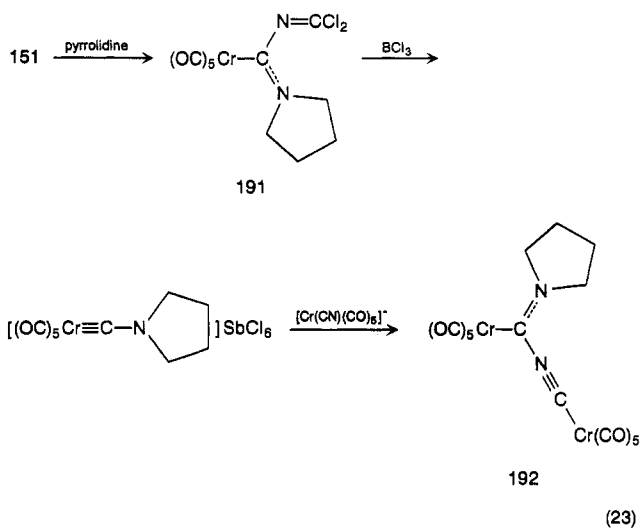


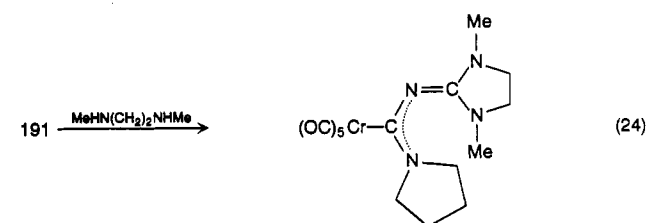
Figure 15. Molecular structure of 172. Important bond lengths (Å) and bond angles (deg): Cr–C1 2.012(4), C1–N1 1.397(3), N1–C7 1.232(4), C1–N2 1.332(4), N2–C8 1.196(4), Mn–C8 1.796(3); C1–N1–C7 127.9(3), C1–N2–C8 172.9(4).³³⁹

for its ability to stabilize carbanions, is also most effective in carbene (carbenium) stabilization thus confirming predictions on this matter made on the basis of MO considerations.^{339,351}

A second route to μ_2 -isocyanocarbene moieties has been developed in which iminocarbene (191) and aminocarbene intermediates are involved (eq 23).³⁵²

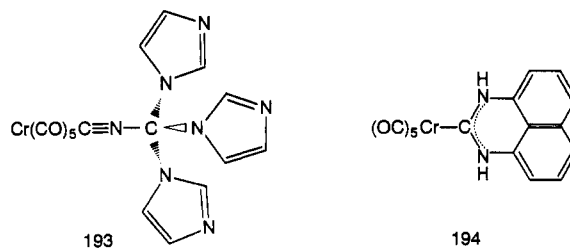


(c) When amine or thiol is used in excess, a second or even third molecule of the nucleophile is incorporated into the azomethyne part of the polyfunctional ligand (cf. 173 and 175, Schemes VII and VIII, and eq 24).^{339,349,350} Some *N*-heterocycles (benzimidazole, azir-



idine) behave similarly, yet imidazole deviates from this reaction scheme in that it forms the tris(imida-

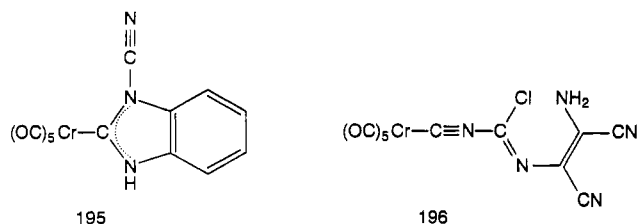
zole)methyl isocyanide complex 193 which is much less electrophilic than 151 yet still able to react with 1 equiv of a stronger nucleophile like pyrrolidine.³⁴⁷



(d) Reactions with HSEt/NEt₃, dithiols, or diamines result in a further degradation of the complex-bound trichloromethyl isocyanide: in the molecules 177–179 (Scheme VII) or 194, only the isocyanide carbon atom is left, i.e., CNCCl₃ reacts like dichlorocarbene (Scheme VIII), which as such is not available in a pentacarbonylchromium complex.³⁵³

The following reaction sequence, alternating between the electrophilic centers C¹ and C³ has emerged in which up to *seven* (!) molecules of nucleophile are consumed by the “superelectrophiles” A–C (Scheme VIII): (1) “carbene addition” of the nucleophile NuH followed by HCl (NuH₂+Cl[−]) elimination; (2) Cl/Nu substitution(s) at C³ of the dichloromethylene group, (3) repeated nucleophilic addition at C¹ and elimination of a carbonic acid derivative HN=C(Nu)₂.

As a deviant from this scheme, *N,N'*-dimethyldiaminoethane adds across both electrophilic C-centers in 151 to give a carbenoid seven-membered triazepane ring system (176) of which the crystal and molecular structures were reported.³⁵³ Exceptional results (195 and 196), not in line with the main reaction patterns, have also been obtained from the reactions of 151 with *o*-phenylenediamine and diaminomaleodinitrile.³⁴⁷



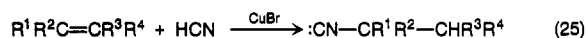
(e) Toward primary amines, complex 151 (and to some extent also 186) again acts as a dichlorocarbene equivalent effecting the spontaneous formation in quantitative yields of a wide variety of isocyanide complexes 180, including those containing sterically demanding, functional, chiral, or divalent isocyanide ligands (see caption to Scheme VII).³⁵⁴ There were earlier reports on similar interconversions of nonfunctional isocyanides which, however, required an auxiliary agent (COCl₂).³⁵⁵ Just like these have been viewed as metal-modified Ugi syntheses, the above process may be described in terms of an organometallic analogue of the Hofmann isocyanide synthesis (from an amine and a dichlorocarbene source) where the Lewis acid component is part of the system.³⁵⁶ Both synthetic routes greatly profit from the stabilizing effect of metal coordination, after all.

C. [M]CN–H Additions to Unsaturated Substrates (Hydroisocyanation)

For hydroisocyanations of small rings (epoxides, aziridines), see III.D.

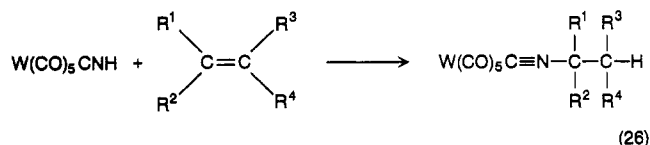
1. Hydroisocyanations of Olefins and Acetylenes

Transition metal-catalyzed hydrocyanations of olefins, cycloolefins, and particularly, diolefins are large scale industrial processes of ever increasing importance.^{12a,12c,357} By way of contrast, there is just one single report on catalytic hydroisocyanations (eq 25) which nevertheless appear economically attractive too, if only because of the readily available starting materials.³⁵⁸



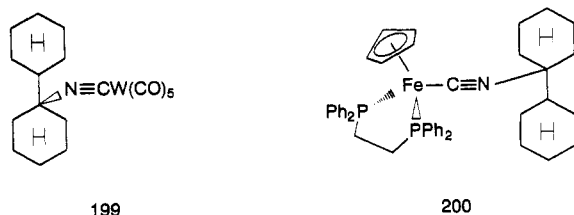
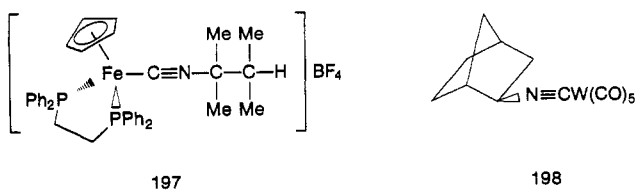
Now the first *stoichiometric* hydroisocyanations of higher alkylated olefins have been carried out with CNH stabilized in various metal compounds and found to provide a direct and convenient access in good yields to alkyl isocyanide complexes. For a further simplification of the synthetic procedure, one can start out directly from the parent cyano complex and the stoichiometric amount of acid (e.g. HBF₄) instead of taking the trouble to isolate the less stable (or nonexisting)(!), cf. section II.A) hydrogen isocyanide complexes.⁶¹

With the strongly acidic W(CO)₅CNH, the reactions are complete within a few hours at room temperature (eq 26). The cationic isocyanide iron complex 197 is



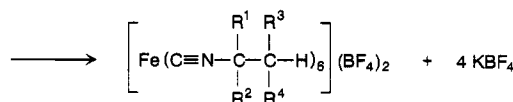
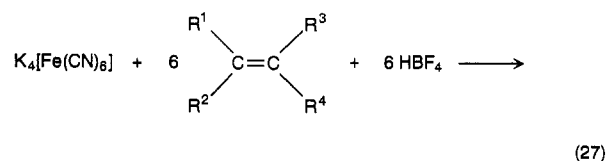
R ¹	R ²	R ³	R ⁴
Me	Me	Me	H
Me	Me	Et	H
Me	Me	Bu ^t	H
Me	Me	Me	Me
Et	Et	H	H

most conveniently prepared from a mixture of Fe(C-N)Cp(dppe), 2,3-dimethylbut-2-ene, and etheral HBF₄. Like in other HX additions, protonation of the olefinic double bond most probably occurs as the primary step of reaction to generate the more stable carbenium ion which subsequently N-alkylates the cyanometalate (cf. section III.A). In all cases, only one regioisomer is formed, i.e. L_nMCNH additions to CC double bonds strictly obey the Markovnikov rule. A product (198) having the expected 2-exo structure arises from W(CO)₅CNH and norbornene.



With cyclohexene, however, the reaction deviates from the general scheme in that two cyclohexene units couple selectively on both, the pentacarbonyl tungsten and the (cyclopentadienyl)(diphosphine)iron fragments, to give the (1-cyclohexyl)cyclohexyl isocyanides 199 and 200 which are unequivocally identified by their ¹H-coupled ¹³C NMR spectra, exhibiting the required one singlet, one doublet, and six triplets.⁶¹ Presumably it is the attraction of the tertiary carbenium ion formed in a dimerization step somewhere in between protonation and N-alkylation which causes this surprising variant.

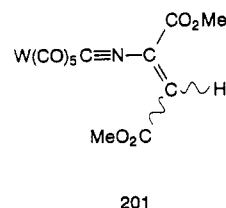
At slightly elevated temperatures (80–100 °C), the system [Fe(CN)₆]⁴⁻/aqueous HBF₄ adds a total of six molecules of olefin per metal atom thus opening up a high-yield route to the class of hexakis(alkyl isocyanide)iron complexes which otherwise is not accessible without difficulties (eq 27).⁶¹ Furthermore, since the



R ¹	R ²	R ³	R ⁴
Me	Me	Me	H
Me	Me	Et	H
Me	Me	Me	Me
Me	Me	H	H
Et	Et	H	H

isocyanide is easily removed from the metal, this procedure should be superior to the established organic route via amines and formamides.

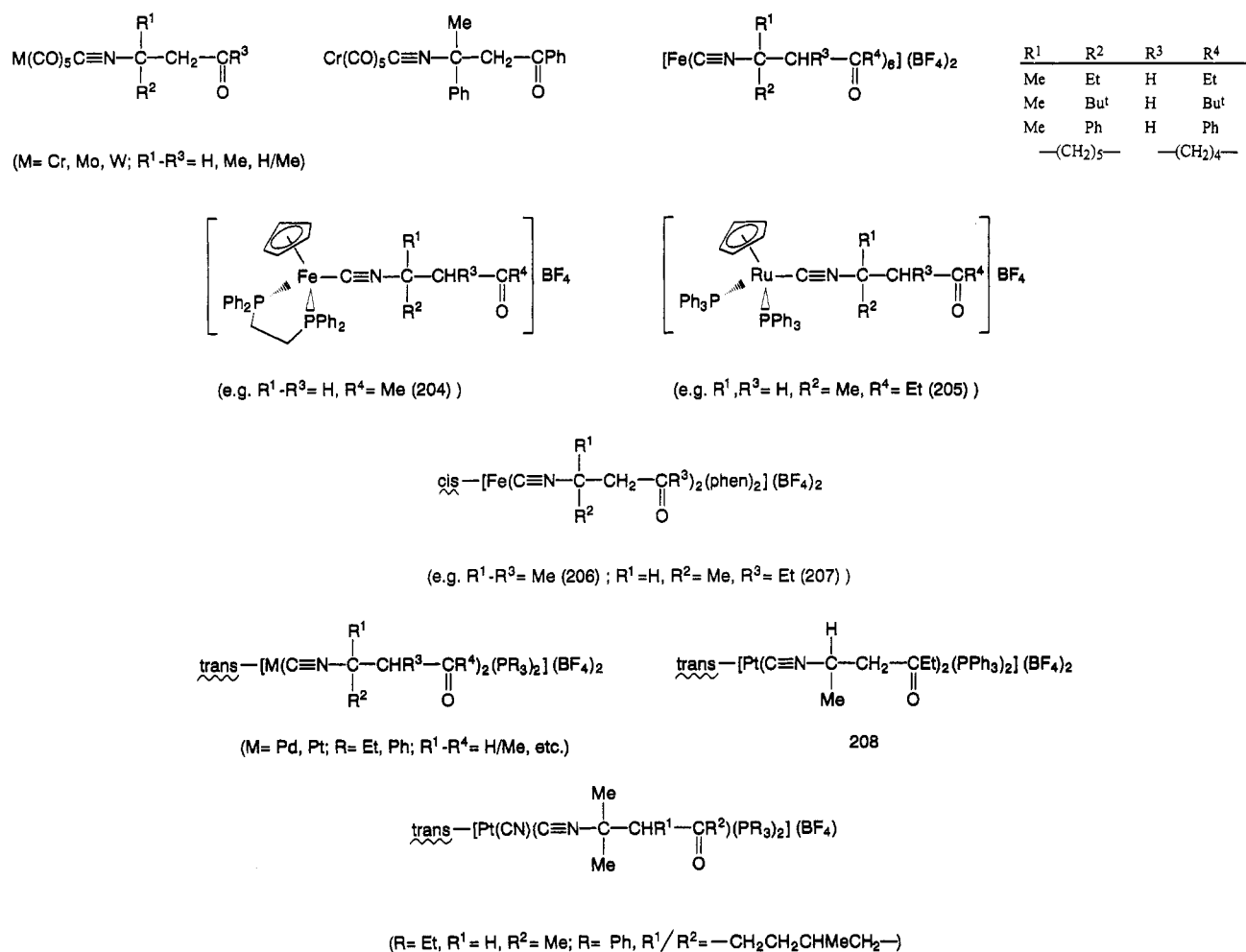
On the other hand, very little is known about L_nMCNH additions to alkynes. Actually, only one experiment has so far been carried out in this field, viz. the reaction of Na[W(CN)(CO)₅] with dimethyl acetylenedicarboxylate and HBF₄ to give the vinyl isocyanide complex 201 which exists as a mixture of the geometric isomers.³⁵⁹



Diverse complexes of vinyl isocyanides (including homoleptic ones) have been prepared from the components.³⁶⁰ Recently, another way of synthesizing vinyl and bisvinyl isocyanides "in the complex" was reported which is based on Wittig-type reactions between the isocyanide complexes L_nMCNCHPPh₃ and carbonyl or dicarbonyl compounds, respectively.³⁴⁶

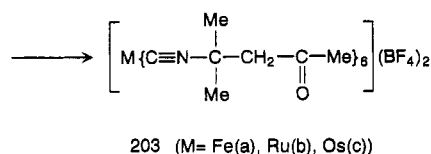
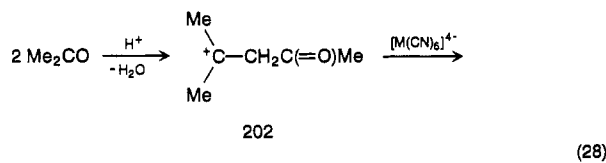
2. Hydroisocyanations of α,β-Unsaturated Carbonyl Compounds. γ-Oxo Isocyanide Complexes

For over 100 years, the alkylation of cyano complexes was the only general reaction at this coordinated ligand. With their fortuitous discovery in 1972 of the ready

Scheme IX. Further γ -Oxoalkyl Isocyanide Complexes (For the Diverse Carbonyl Components Employed, See the Text!)

addition of L_nMCNH or L_nMCN/H^+ to various α,β -unsaturated ketones, Beck and Schaal actually initiated the organometallic chemistry of cyanide which we deal with in this paper.³⁶¹

On the attempted alkylation of hexacyanoferrate with oxonium salt in acetone, a cationic hexakis(alkyl isocyanide) complex with keto functions in the 3-positions (relative to the isocyano group) arose in high yields. This was explained by an acid-catalyzed aldol condensation of acetone and trapping of the resulting tertiary carbenium ion **202** through its bonding to the nucleophilic cyano-N atom (eq 28). In fact, it has been



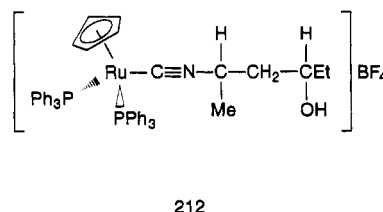
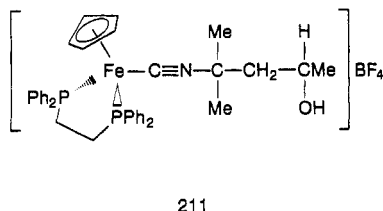
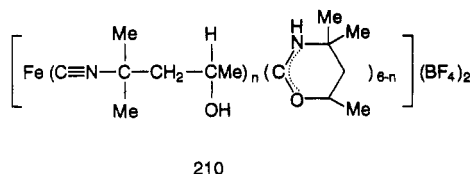
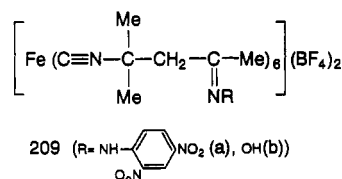
shown that **203a** can almost quantitatively be obtained by reaction of $K_4[Fe(CN)_6]$ and 4-hydroxy-4-methyl-2-pentanone or 4-methyl-3-pentene-2-one (mesityl oxide) in aqueous HBf_4 .

Both, the organic carbonyl and the cyanometal components have then extensively been varied to include the ketones methyl ethyl ketone, isobutyl methyl ketone, cyclohexanone, and acetophenone as well as the α,β -unsaturated ketones 3-butene-2-one, 1-pentene-3-one, 4-hexene-3-one, 2-cyclohexene-1-one, phorone (2,6-dimethyl-2,5-heptadiene-4-one) and (*R*)-(+)-pulegone [(*R*)-(+)-*p*-menth-4(8)-ene-3-one] on the one side, and the hydrogen isocyanide/cyano complexes $M(CO)_5CNH$ (M = Cr, Mo, W), *cis*- $Fe(CN)_2(phen)_2$, $Fe(CN)Cp(dppe)$, $Ru(CN)Cp(PPh_3)_2$, and *trans*- $M(CN)_2(PR_3)_2$ (M = Pd, Pt) on the other.^{359,362,363} Also, one α,β -unsaturated aldehyde (acrolein, acroleindiethyl acetal) has been subjected to this reaction; $Cr(CO)_5-CNSiMe_3$ has successfully been employed as a CNH complex equivalent.³⁵⁹

A survey of the γ -oxoalkyl isocyanide complexes that have been synthesized in addition to **203** is given in Scheme IX.

Subsequent reactions have been carried out at the keto functions which according to an X-ray structure of **203a** all lie at the surface of the sphere-shaped complex cation.³⁶² All six carbonyl groups could be derivatized with (2,4-dinitrophenyl)hydrazine and hydroxylamine to give **209a** and **209b** and reduced with $NaBH_4$ in the presence of $CeCl_3 \cdot 6H_2O$ in methanol/dichloromethane to give **210** which results from partial isomerization to carbenoid-bound oxazolidines of the functional isocyanide within the coordination sphere

of the hexakis(γ -hydroxyalkyl isocyanide)iron intermediate (see section III.D).³⁶² Partial cyclization of the γ -hydroxy isocyanide ligands was also observed in the reduced forms of **206** and **207**. Reduction of the keto group in **204** and **205**, on the other hand, led to the "open-chain" hydroxy isocyanide complexes **211** and **212**, respectively, the latter existing as a 3:2 mixture of diastereoisomers.³⁶³

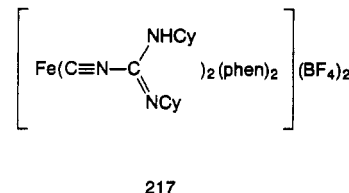
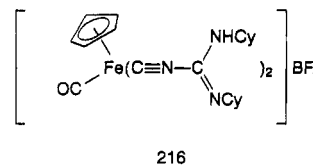
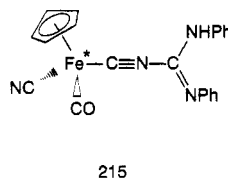
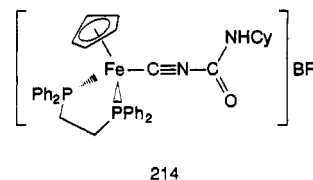
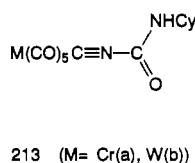


During reduction, occasionally, some of the γ -hydroxy isocyanide is cleaved off the metal; in other cases, reformation of the α,β -unsaturated ketones was noticed. A quantitative retro-Michael addition to give $\text{Pt}(\text{CN})_2(\text{PPh}_3)_2$ and the corresponding hexenone was observed in the reduction of complex **208**.³⁶³

Similar observations have been made on the attempted thermal cleavage of the metal-functional isocyanide bond which thus, unlike the alkylisocyanides derived from higher alkylated olefins (cf. section III.C.1), are not accessible as free species via their organometallic synthesis.³⁶²

3. Additions of CNH Complexes of Chromium, Tungsten, and Iron to Heteroallenes

The hydrogen isocyanide complexes generated "in situ" from $\text{NEt}_4[\text{M}(\text{CN})(\text{CO})_5]$ ($M = \text{Cr}, \text{W}$) and $[\text{Fe}(\text{CN})\text{Cp}(\text{dppe})]$ using ethereal HBF_4 react with an excess of cyclohexyl isocyanate to yield the metal-stabilized isocyano carboxamides **213** and **214**.³⁶⁴ *N,N*-Dialkylated derivatives thereof have recently been obtained by reaction of $\text{Cr}(\text{CO})_5\text{CNCCl}_3$ with secondary amines and subsequent hydrolysis on silica.³⁴⁹ Direct carbamoylation of $[\text{Cr}(\text{CN})(\text{CO})_5]^-$ with R_2NCOCl was unsuccessful, however.



Special spectroscopic features of the new functional isocyanides comprise strikingly low IR frequencies of the CN vibrations (e.g. **214** 2012 s, br cm^{-1}), low-field ^{13}C NMR signals for the isocyano carbon atoms (e.g. **213a**, δ 183.2; **214**, δ 187.5 t), and high intensity lines in the mass spectra for the ions $[\text{M}(\text{CO})_n\text{CNH}]^+$ ($n = 5-0$) and $[\text{CyNCO}]^+$, the latter indicating the main fragmentation to proceed via a reversal of formation.

Hydroisocyanation of carbodiimides has similarly been accomplished to give the isocyano-amidine complexes **215-217**, while in the reactions with $\text{Ru}(\text{CN})\text{Cp}(\text{PPh}_3)_2$ or *trans*- $\text{Pt}(\text{CN})_2(\text{PPh}_3)_2$ trimerization of the heteroallene prevails.³⁶⁴

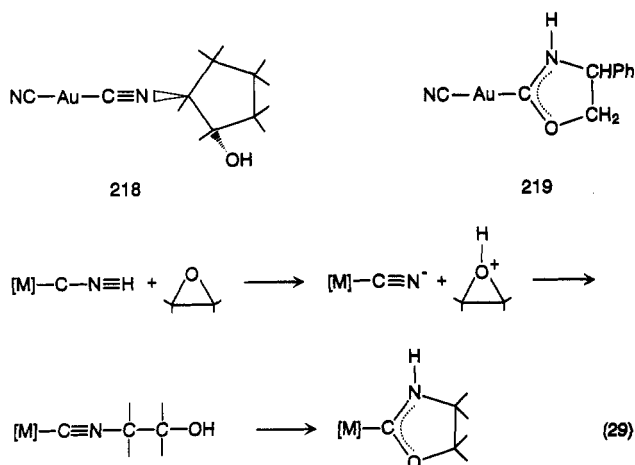
D. Cycloadditions

1. Reactions of Cyanometal Acids with Epoxides

The earliest reports on this kind of experiment date back as far as 1901 when von Baeyer and Villiger became interested in the reaction of $\text{H}_2\text{Fe}(\text{CN})_6$ with ethylene oxide in connection with their investigations of the "basic properties of oxygen".³⁶⁵ It was not until 1984 that Beck et al. resumed and, fortunately, extended this study to also include the cyano acids of the higher homologues of iron as well as those of platinum(II) and gold(I).³⁶⁶ For, while in the iron group only nonreproducible mixtures of up to seven complex species, containing unreacted cyano groups and 2-hydroxyalkyl isocyanides besides longer chain isocyanides (presumably from epoxide oligomerization), "yet certainly no cyclic carbenes"(!) have been obtained,³⁶⁷ $\text{Au}(\text{CN})\text{CNH}$ and $\text{Pt}(\text{CN})_2(\text{CNH})_2$ gave rise to well-defined 2-hydroxyalkyl isocyanide, e.g. **218**, and oxazolidin-2-ylidene complexes, e.g. **219**. An X-ray structure analysis of **219** has been carried out³⁶⁶ which served as a basis for the structural assignment, e.g. of **220** as the α -phenyl derivative (see also below).³⁶⁸

Ring opening of the epoxide presumably proceeds by nucleophilic attack of the cyano-N atom at the O-protonated heterocycle (eq 29), i.e. by a mechanism which is well established for other HX additions to oxiranes.³⁶⁹

The open-chain hydroxy isocyanides, primary products in this reaction sequence, are either stable isolable substances or spontaneously rearrange to cyclic *N,O*-



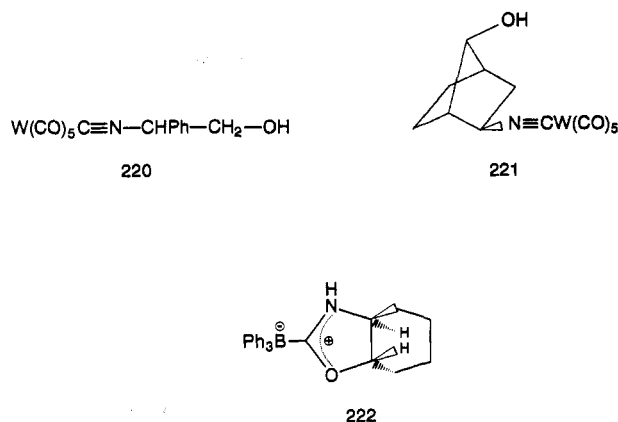
carbenes through an intramolecular 1,2-addition of the hydroxy function across the CN triple bond. A series of studies dealing with the organometallic chemistry of 2- and 3-hydroxyalkyl isocyanides has shown this isomerization to occur primarily as a function of the metal to which the isocyanide is bonded.³⁷⁰⁻³⁷⁴ An influence of the other ligands and of the substitution pattern of the side chain of the isocyanide has also been observed (see below).

In the case of 218 and its cyclohexane analogue, however, it is the stereochemically unfavorable orientation of the isocyano and hydroxy groups relative to each other resulting from the trans-diaxial ring opening of the bicyclic epoxides which has been made responsible for the absence of the cyclization.³⁶⁶ From $\text{W(CO)}_5\text{CNH}$ and 2,3-epoxynorbornane the bicyclic hydroxy isocyanide 221 was synthesized and assigned the shown structure on the basis of an excellent agreement between the ^{13}C chemical shifts calculated for this (2-*exo*-7-*syn*) isomer from the values of pentacarbonyl(2-*exo*-isocyanonorbornane)tungsten (see section III.C.1) and the experimental data of 221.³⁶⁸ (The major product of the reaction of *endo*-2,3-epoxy-1,7,7-trimethylbicyclo[2.2.1]heptane with $\text{Me}_3\text{SiCN/ZnI}_2$, on the other hand, was unequivocally established by single-crystal X-ray analysis to be the *anti*-7-(trimethylsiloxy)-*exo*-2-isocyanano isomer resulting from a classical cationic rearrangement of the bicyclo[2.2.1]heptyl skeleton.³⁷⁵)

"Open-chain" 2-hydroxycyclohexyl isocyanide ligands have also been generated at ruthenium(II) by reacting $\text{Ru(CN)Cp(PPh}_3)_2$ with cyclohexene oxide and tetrafluoroboric acid-etherate¹²⁶ and at tungsten(0) where nucleophilic additions to the isocyano group generally do not take place for electronic reasons.³⁶⁸

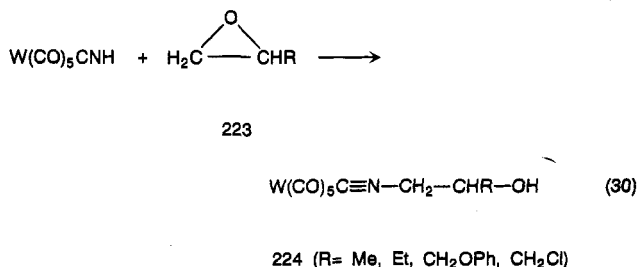
At BPh_3 , in contrast, ring closure occurred on ethanolysis of the trans-diaxial 2-(trimethylsiloxy)cyclohexyl isocyanide to give the "boron-stabilized" bicyclic *N,O*-carbene 222 which demonstrates the accessibility, in principle, even of strained systems of this type if only the isocyano group is sufficiently activated by the "metal".^{376,377}

For the synthesis of "free" 2-hydroxy isocyanides, a new highly stereospecific and largely regioselective route was developed by Gaussman and Guggenheim as well as by Spessard et al., which involves the opening of epoxides with trimethylsilyl cyanide-zinc halide.^{378,379} Accordingly, opening of oxetanes with the same reagent gave γ -trimethylsiloxy isocyanides³⁸⁰ and, on hydrolysis, γ -amino alcohols, constituting a general approach to this class of compounds.³⁸¹ Much better yields of



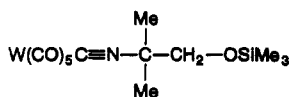
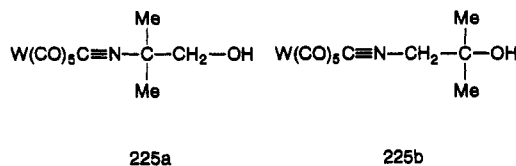
2-trimethylsiloxy isocyanides were obtained under the catalytic action of the soft Lewis acids Pd(CN)_2 , SnCl_2 , and GaMe_3 .^{202c} Interestingly, catalysis by aluminum chloride, diethylaluminum chloride, aluminum alkoxides, or ytterbium tricyanide gave rise to an entirely different type of product, namely the trimethylsilyl ether of β -hydroxynitriles, and it was speculated on the intermediacy of Et_2AlNC in the latter as against XZnCN ($\text{X} = \text{Cl, I}$) in the former case.^{202c,379,382,383} Both, the site of attachment, N or C, of the ambident cyanide and the regiochemistry which, too, was reversed on merely changing the Lewis acid catalyst seem to be wholly governed by HSAB principles.³⁸⁴

It is a surprise that the regiochemistry associated with the isocyanide formation from epoxides and $\text{Me}_3\text{SiCN/ZnX}_2$, Pd(CN)_2 , SnCl_2 , or GaMe_3 , viz. the preferential entry of CN at the higher substituted carbon of unsymmetrical oxiranes ("anomalous product"),³⁶⁹ is reversed in the reactions of $\text{W(CO)}_5\text{CNH}$ with the monoalkylated epoxides 223. In general, regiospecific ring opening occurred to give the corresponding 2-hydroxyalkyl isocyanide complexes 224 (eq 30), except with 1,1-dimethyloxirane which gave rise to



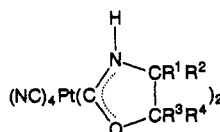
a 3:1 mixture of regioisomers 225a,b. Similarly, 1:1-isomeric mixtures of metal-bonded 2-(trimethylsiloxy)-alkyl isocyanides (e.g. 226a,b) and, through their rapid hydrolysis, again 2-hydroxyalkyl isocyanides have been obtained starting out from $\text{M(CO)}_5\text{CNSiMe}_3$ ($\text{M} = \text{Cr or W}$).³⁶⁸

The reactions of HAu(CN)_2 , $\text{H}_2\text{Pt(CN)}_6$, and $\text{H[Co(CN)}_2(\text{dmgH})_2]$ with 1,1-dimethyl-substituted oxiranes also lead to mixtures of isomers, this time, however, of the cyclized oxazolidin-2-ylidene complex type. In case of the platinum(IV) complexes 227a-c, a particularly complicated situation exists as in addition to the regioisomers, *cis-trans* isomers and even *RR(SS)/RS(SR)* diastereoisomers have to be taken into account. Actually, as many as seven carbene carbon signals have been detected in the ^{13}C NMR spectrum of 227b/227b'. Nevertheless, it was possible to crystallize a single



226a (+226b, regioisomer)

isomer and to obtain a rare X-ray structure of a rare platinum(IV) carbene complex (Figure 16).³⁸⁵

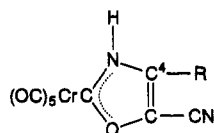


	R ¹	R ²	R ³	R ⁴
227a	Me	Me	H	H
227a'	H	H	Me	Me
227b	Me	Me	COMe	H
227b'	COMe	H	Me	Me
227c	Me	Me	CO ₂ Et	H
227c'	CO ₂ Et	H	Me	Me

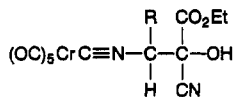
Rather different results have been obtained with the novel class of *gem*-dicyano and cyanocarbethoxy epoxides 228 which due to their "dielectrophilic" reactivity can be viewed as ketenyl cation synthetic equivalents.³⁸⁶ In the reactions with hydrogen isocyanide complexes, however, 228a and 228b, at least formally, behave more like 1,3-dipoles of the type of ketocarbenes,³⁸⁷ taking up only one molecule of nucleophile to give the cycloaddition products 229. The alternative regioisomers with the CN group on C⁴ have been ruled out on spectroscopic grounds (see, however, below).



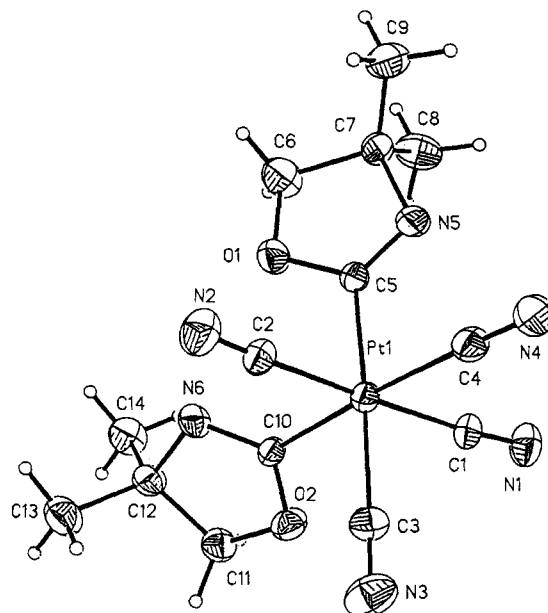
228 (X = CN, R = 4-MeC₆H₄(a)
or 4-ClC₆H₄(b);
X = CO₂Et, R = 4-ClC₆H₄(c))



229 (R = 4-MeC₆H₄(a)
or 4-ClC₆H₄(b))

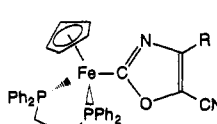
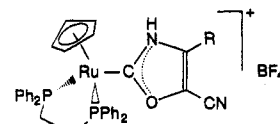
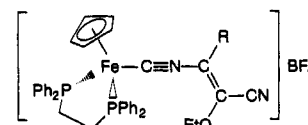
230 (R = 4-ClC₆H₄)

That actually the hydroxyalkyl isocyanide step is passed was made evident by the isolation from the reaction of Cr(CO)₅CNH with 228c of the metastable intermediate 230. Within hours, solutions of 230 develop ¹³C signals at 223 and 113.5 ppm which are indicative of the final products carbene and HCN, respectively.^{388,389} This raises again the question as to the factors controlling this hydroxyalkyl isocyanide to *N,O*-carbene isomerization which obviously is also very sensitive even to subtle changes in the side chain of the hydroxy isocyanide. In the special case of 230, the

Figure 16. Molecular structure of 227a.³⁸⁵

stability of the "open" form has tentatively been connected with the unfavorable conformation, *cis*-(C⁴)H/(C⁵)CN, for HCN elimination from a primary cyclization product.³⁸⁸

Analogous reactions have been carried out with the cyano complexes M(CN)Cp(dppe) (M = Fe, Ru) and the corresponding cationic hydrogen isocyanide derivatives prepared "in situ". As products resulted, neutral oxazolato (e.g. 231) or oxazolin-2-ylidene (carbene) complexes (e.g. 232), respectively, which could be transformed into each other by protonation/deprotonation.

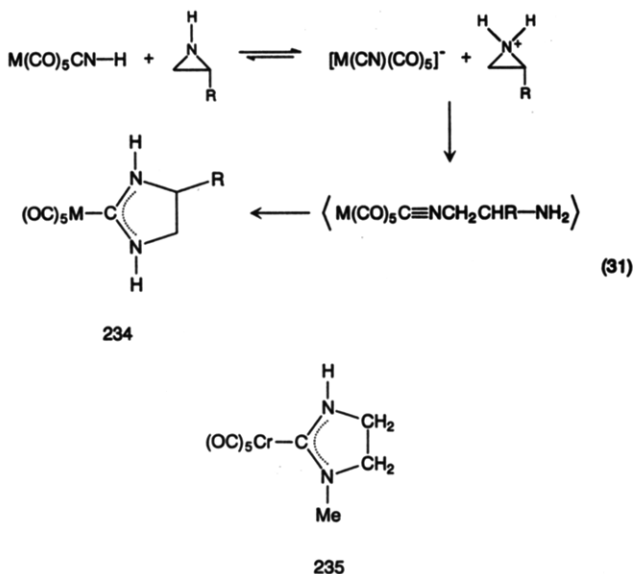
231 (R = 4-ClC₆H₄)232 (R = 4-ClC₆H₄)233 (R = 4-ClC₆H₄)

Action on type 231 compounds of trialkyloxonium salts unexpectedly caused ring opening with formation of highly functionalized vinyl isocyanide iron and ruthenium complexes. The structural details of one, 233, have been established by X-ray analysis and found to be in full accord with the structures assigned earlier to the heterocyclic precursor ligands.³⁸⁹

2. Cyclic Diaminocarbene Complexes

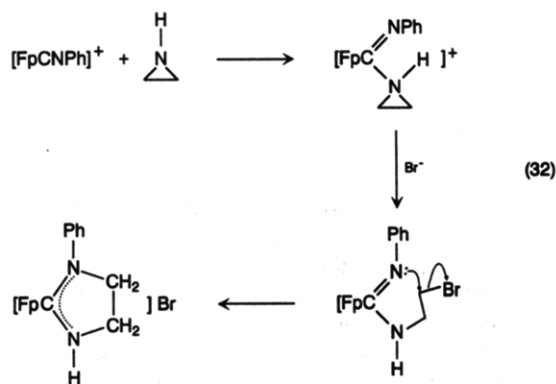
Aziridines have been reacted with the hydrogen isocyanide complexes M(CO)₅CNH (M = Cr, Mo, W) or, more conveniently, [M(CN)(CO)₅]⁻ followed by addition of HBF₄ to give the compounds 234 and 235 in low yields.³⁹⁰

A plausible mechanism comprising the steps (a) protonation of the aziridine, (b) ring opening through



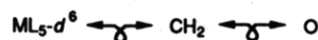
nucleophilic attack by the nitrogen atom of the anionic cyano complex, and (c) immediate cyclization of the transient 2-aminoalkyl isocyanide is outlined in eq 31. Parallels may be drawn between this procedure and the halide-promoted syntheses of cyclic aminooxo-, dioxo-, and diaminocarbene complexes from metal carbonyls or isocyanides on the one side, and aziridines or oxiranes, respectively, on the other.³⁹¹

Mechanistically, however, a major difference is to be stated in the reverse order of the central steps of N-alkylation and carbene addition (eq 32).³⁹⁰



3. Four-Component Condensations and Three-Component Additions

The use of cyanic acid (HOCN) or thiocyanic acid (HSCN) as the acid component in Ugi's four-component condensation reactions had opened an attractive synthetic access to five-membered heterocycles of the hydantoin type, viz. hydantoin imides and thiohydantoin imides.³⁹² Such compounds are potentially biologically active substances for the synthesis of which numerous procedures have been developed including two organometallic ones.^{393,394} Encouraged by the isolobal relation³⁹⁵



Fehlhammer et al. have started to look at 4CC's with hydrogen isocyanide complexes in the place of HNCO, and this subsection reports some preliminary results from these studies.³⁹⁶⁻³⁹⁸

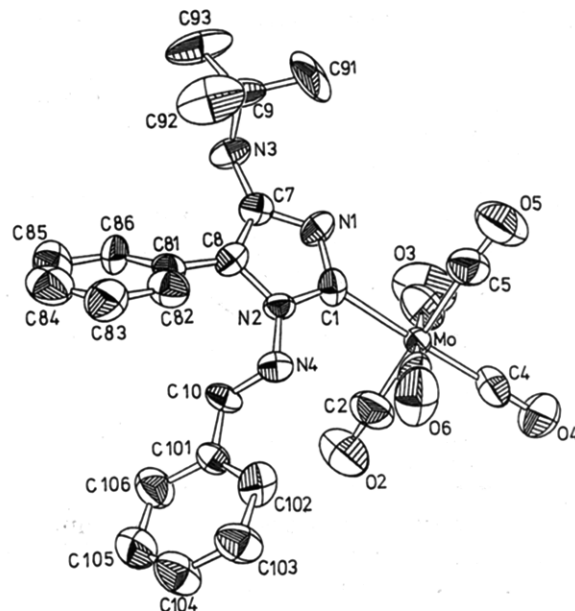
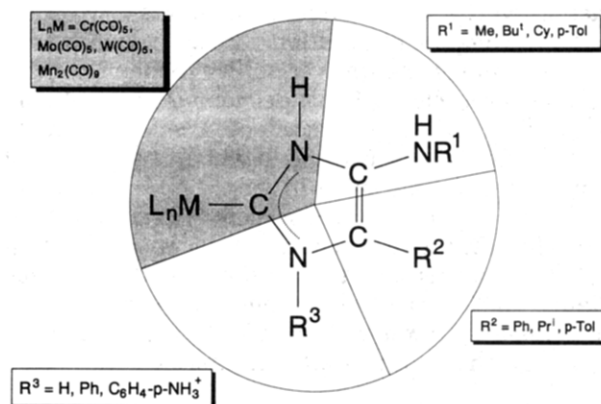
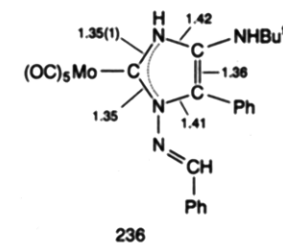


Figure 17. Molecular structure of 236.

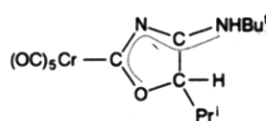
Scheme X. Four-Component Condensations with Cyano Complexes



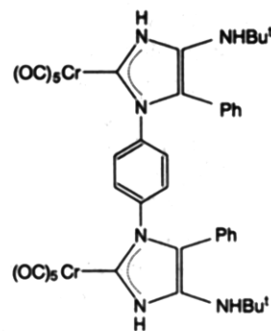
The components were mixed in the order CNH complex, aldehyde, isocyanide, amine, and allowed to react for a few hours on the average. Workup then gave the expected C-bonded imidazolin-2-ylidene ligand carrying an amino substituent in position 4 (Scheme X). The structure was ascertained by NMR (¹H, ¹³C) and mass spectrometry data as well as by an X-ray study of a 4CC product (236) with hydrazine in lieu of the amine (Figure 17). Diamines give rise to dinuclear



236

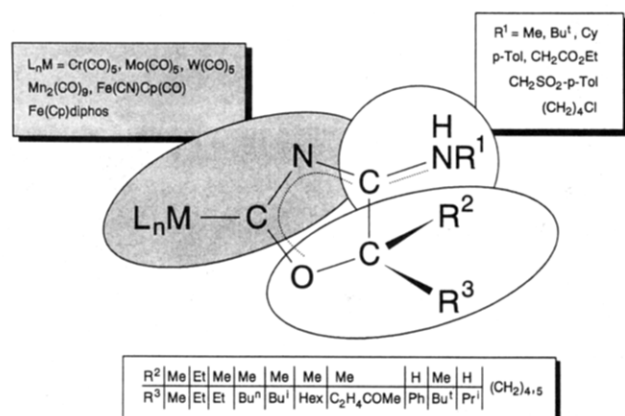


238



237

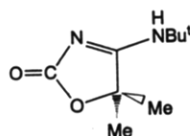
Scheme XI. Three-Component Additions with Cyano Complexes



species such as **237**. Note that in the procedure the CNH complex can conveniently be replaced by the corresponding cyano complex if the required stoichiometric amount of acid is provided in form of amine hydrochloride.

In the 4CC's with hydrazine, side products were observed, e.g. **238**, in the formation of which hydrazine was obviously not involved. Hence, another novel reaction type of coordinated cyanide was discovered, the three-component addition ("3CC") which turned out to be of even greater variability (Scheme XI).

The heterocycle—a C-bonded nonaromatic 4-aminoxazoline with an unprecedented π -delocalization along the O–C–N–C–N_{exo} chain which is also evident from severe low-field shifts in the ^{13}C NMR spectra of the C2 and C4 carbon atoms—can be cleaved off the metal by oxidative decomposition with $\text{KMnO}_4/\text{Fe}(\text{NO}_3)_3$. In this way, the oxazolinone **239** has been obtained in 60% yield which compares favorably with the necessarily lower yield ($\sim 25\%$) of the multistep organic synthesis of this effective herbicide.³⁹⁹



239

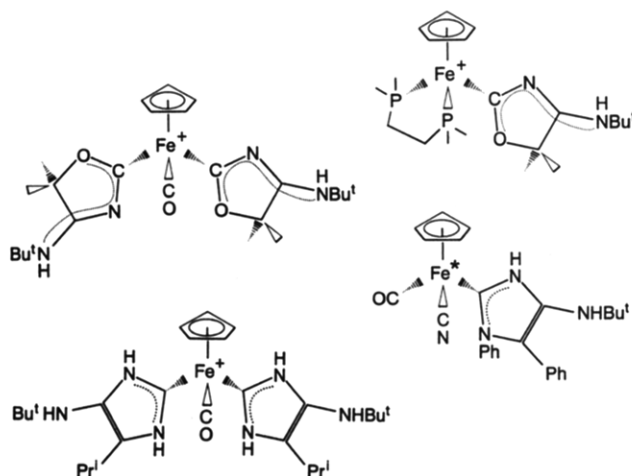
The general validity of these reactivity patterns (Schemes X and XI) for metal cyanides is demonstrated by the successful incorporation of cyanoiron(II) and -cobalt(III) species in the 3CC and 4CC chemistry (cf. Scheme XII and XIII).

E. Cleavage of the CN Triple Bond of the Coordinated Ligand

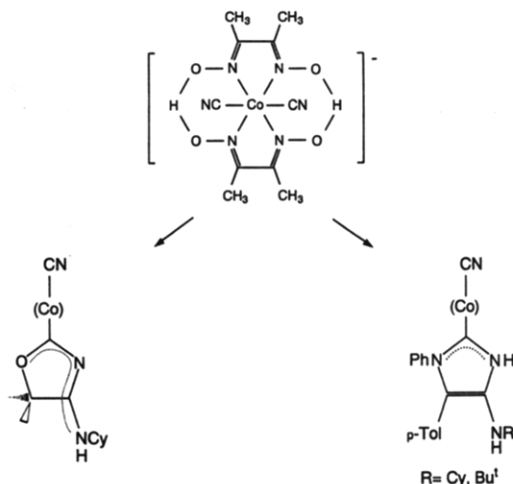
The mobility of the cyano ligand in small clusters such as $[\text{Fe}_2(\text{CN})\text{Cp}_2(\text{CO})_3]^-$ or $[\text{Os}_3(\text{CN})(\text{H}_2)(\text{CO})_{10}]^-$ (cf. section II.B) opens up new possibilities for its chemistry.^{57,158} For the first time reactions can also occur at CN in the bridging position where the N-nucleophilicity is drastically increased.

Protonation and alkylation of the terminal CN ligand of $[\text{Fe}_2(\text{CN})\text{Cp}_2(\text{CO})_3]^-$ had led directly to the bridging aminocarbene ligands CNH_2^+ and CNR_2^+ , respectively; monoprotection to give CNH had proven impossible (see section II.A) and monoalkylation to give the isocyanide could only be achieved with bulky alkyl

Scheme XII. Cyanoiron(II) Complexes in Three- and Four-Component Condensations



Scheme XIII. Cyanocobalt(III) Complexes in Three- and Four-Component Condensations



groups. (In this respect, the diiron system differs remarkably from the cyanodimanganese A-frame (section II.D) and the cyanotriosmium cluster (section II.A) both of which have been reported to form μ_2 -CNH species on protonation.^{42,57,252})

Acylation of $[\text{Fe}_2(\text{CN})\text{Cp}_2(\text{CO})_3]^-$ ($\equiv [\text{Fe}_2]\text{CN}^-$), on the other hand, only gave μ -(monoacyl) isocyanide complexes, even when the acylating agent was applied in excess;³⁰² dicarboxylic acid chlorides, accordingly, reacted in a 1:2 fashion thus giving rise to bis(μ -acyl isocyanide diiron) species (cf. section III.A.2, 117 and 118). The reaction with phthaloyl dichloride, however, followed a completely unexpected course culminating in the aprotic cleavage of the CN triple bond under very mild conditions and the fixation of the resulting μ -carbidoiron fragment to a second cyanodiiron complex anion (eq 33). Various salts (BF_4^- , PF_6^- , ClO_4^- , BPh_4^-) of the unique tetranuclear cation **240** have been prepared by anion exchange. According to an X-ray structure analysis (Figure 18) **240** is composed of two cis-configured $\text{Fe}_2\text{Cp}_2(\mu\text{-CO})(\text{CO})_2$ units which are linked through an almost linear (C7–N–C8 172.3(9)°) CNC bridge.³⁰⁵ Identical C7–N (1.24(1) Å) and C8–N (1.24(1) Å) distances of typical CN double bond length, as well as an angle of 87.1(1)° between the Fe1–Fe2–C7–N and Fe3–Fe4–C8–N planes have been taken as justification for the formulation of **240** as a tetrametalated azaallene species. A C_2 axis passing through

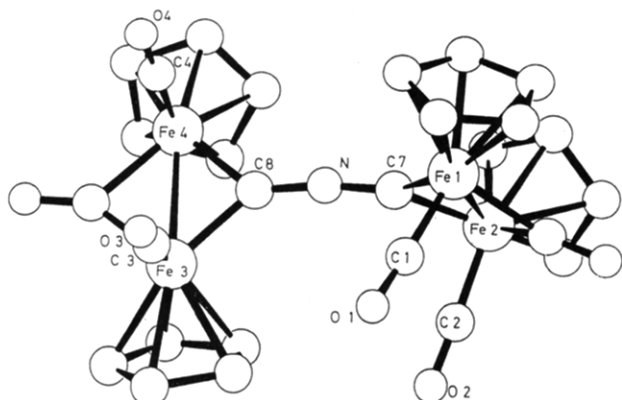
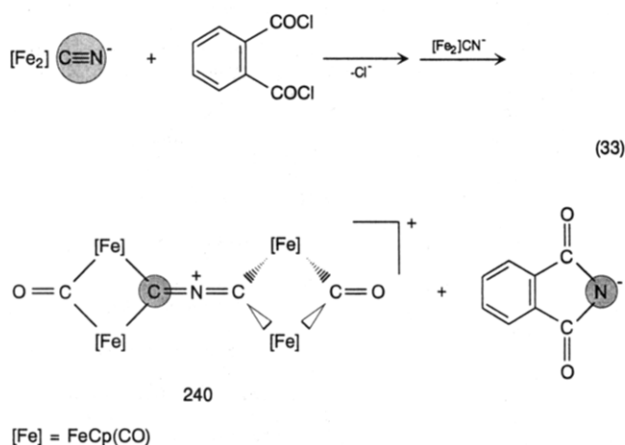
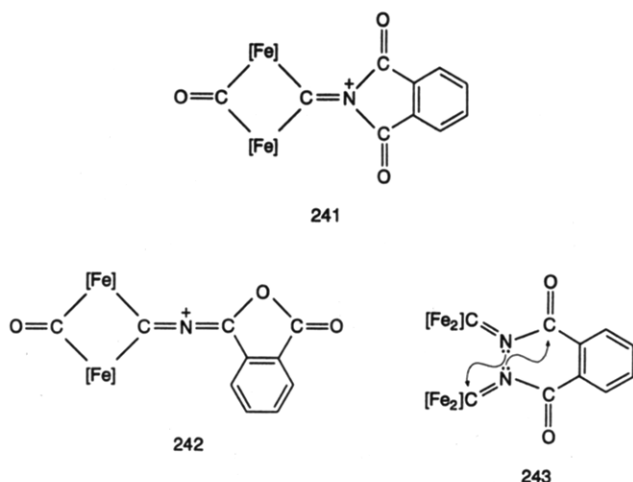


Figure 18. SCHAKAL drawing of the complex cation 240.³⁰⁵

the central N atom is the only (although not crystallographic) symmetry element of the axially chiral cation which thus possesses *two* sets of equivalent Cp and terminal CO ligands. As this is exactly what has been observed in the ^1H and ^{13}C NMR spectra, the structure is obviously retained in solution.

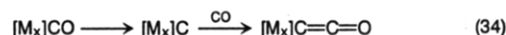


Concerning the mechanism of formation of 240, several intermediates 241–243 have been discussed of which at present the diacylated cyano bridge 241 is the most favored; in fact, this compound for which a

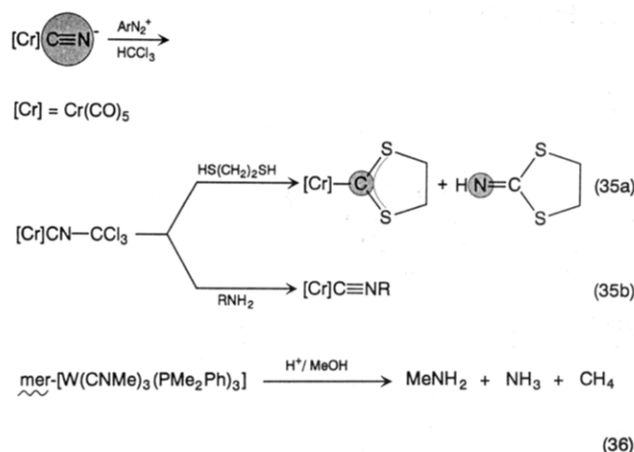


dramatically elongated $\mu\text{-C-N}$ bond might be predicted has very recently been obtained by slow addition of $\text{Na}[\text{Fe}_2(\text{CN})\text{Cp}_2(\text{CO})_3]$ to a large excess of phthaloyl dichloride and shown to react with $[\text{Fe}_2(\text{CN})\text{Cp}_2(\text{CO})_3]^-$ to give 240.⁴⁰⁰

Furthermore, interesting parallels can be drawn between this novel reaction of coordinated CN and certain transformations of CO (and HCN?)⁴⁰¹ in multi-nuclear clusters and on surfaces as studied particularly in connection with the Fischer-Tropsch synthesis. There, reaction sequences are encountered such as the one depicted in eq 34 which clearly reflect the fundamental analogy with the chemistry of CN^- outlined in eq 33.⁴⁰²



It should be recalled that in reaction sequences of the type treated in sections III.B.3d and e (eq 35), even the CN triple bond of *terminal* cyano ligands has successively been broken [and newly generated (eq 35b)] while fully retaining the metal-carbon bond. Finally, despite basic chemical differences, parallels can be drawn to Pombeiro's *reductive* cleavage of the CN bond of isocyanides activated by a single electron-rich metal center (eq 36).⁴⁰³



IV. Concluding Remarks

It is now firmly established that, contrary to a widespread prejudice, CN^- in combination with suitable metal complex fragments is a versatile reagent on which an extensive organometallic chemistry can be based. Although CN^- , unlike carbon monoxide, is not a priori susceptible to nucleophilic attack at the carbon atom—an essential for the development of an organic chemistry of this ligand—there are now strategies to force nucleophilic attack by prior activation. One is the classical ionic alkylation of cyano complexes implying that the organometallic chemistry of cyanide in general proceeds via isocyanides, preferentially functional ones which profit from the stabilizing effect of metal coordination. Closely related in a mechanistic sense are the addition reactions of CNH complexes to unsaturated systems, small rings, etc. to give novel functional isocyanides and, subsequently, cyclic carbene complexes. So are the more component cycloadditions in which electrophilic and nucleophilic additions presumably occur shortly one after the other.

Particularly, strong to extreme activation is achieved by "radical alkylations" of cyano complexes in halo-carbons or by acylation with dicarboxylic acid chlorides (phthaloyl dichloride). So activated, cyanide is capable of "consuming" several molecules of nucleophile which frequently leads to a cleavage of the CN triple bond

under very mild conditions. Also note that it represents convenient readily available C_1 , C_1N_1 , and CNC syntheses for syntheses of heterocycles of immediate interest.

V. Acknowledgments

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VI. Abbreviations

Ar	aryl group
Bu ^t	<i>tert</i> -butyl
bipy	2,2'-bipyridyl
cod	1,5-cyclooctadiene
Cy	cyclohexyl
dienEt ₄	1,1,7,7-tetraethyldiethylenetriamine
DMF	dimethylformamide
dmgH	dimethylglyoximate(1-)
DMSO	dimethyl sulfoxide
dppe	1,2-bis(diphenylphosphino)ethane
dppm	1,2-bis(diphenylphosphino)methane
Et	ethyl
L	neutral ligand
LA	Lewis acid
LB	Lewis base
[M]	metal complex fragment
Me	methyl
<i>o</i> -Tol	<i>o</i> -tolyl
Ph	phenyl
phen	<i>o,o'</i> -phenanthroline
Pr ⁱ	isopropyl
Pr ⁿ	<i>n</i> -propyl
R,R'	organyl(alkyl) group
THF	tetrahydrofuran

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