Coordination Chemistry Reviews, 129 (1994) 157–193

The coordination chemistry of TCNE, TCNQ and related polynitrile π acceptors

Wolfgang Kaim and Michael Moscherosch
Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70550 Stuttgart (Germany)

(Received 6 November 1992)

CONTENTS

ABSTRACT

Conjugated polynitriles such as TCNE or TCNQ can act as non-chelating polydentate ligands towards metal centres. Among the outstanding features of these ligands are (a) their propensity to undergo π/π stacking, (b) their non-innocent nature, i.e. their facile interconversion between three oxidation states, including a spin-bearing radical form, (c) their σ/π coordination ambivalence towards metals, and (d) their ability to bridge several metal centres, thus giving rise to oligonuclear complexes and coordination poly-

---

Correspondence to: W. Kaim, Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70550 Stuttgart 80, Germany.

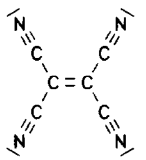
mers. This article contains a survey of the structural and electronic features of metal complexes with TCNE, TCNQ and some related molecules. Guidelines are given to elucidate the type of coordination using vibrational data and to assign reasonable oxidation states to the redox-active polynitrile ligand; close-lying ligand π^* MOs and d orbitals of coordinated transition metals can cause considerable orbital mixing. Attempts are made to relate coordination modes with electronic structures. Electron transfer dominates the chemical reactivity of the polynitriles and of their complexes, various consequences of initial electron transfer such as isomerization, polynucleation or substitutional rate enhancement are discussed. Interesting physical properties resulting from the extended π conjugation in metal complexes of the polynitrile ligands are briefly referred to by example of electrical conductivity, magnetic coupling and long-wavelength optical absorption.

ABBREVIATIONS

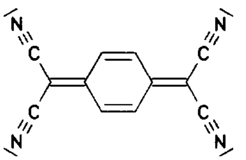
abpt	4-amino-3,5-bis(2-pyridyl)-1,2,4-triazole
acacen	*N*,*N*′-ethylenebis(acetylacetoniminato) dianion
bdpa	bis(3-dimethylarsinopropyl)phenylarsine
bpy	2,2′-bipyridine
Cp	cyclopentadienide $(C_5H_5)^-$
Cp*	pentamethylcyclopentadienide $(C_5Me_5)^-$
DCNQI	*N*,*N*′-dicyano-*p*-benzoquinonediimine
diop	4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane
2,5-DMDCNQI	2,5-dimethyl-*N*,*N*′-dicyano-*p*-benzoquinonediimine
dmpae	1,2-bis(methylphenylarsino)ethane
dmpe	1,2-bis(dimethylphosphino)ethane
2,9-dmphen	2,9-dimethyl-1,10-phenanthroline
dppe	1,2-bis(diphenylphosphino)ethane
Fc	ferrocene
HCBD	hexacyano-1,3-butadiene
hfacac	hexafluoroacetylacetonato
h.s.	high spin
l.s.	low spin
MeCp	methylcyclopentadienide $(C_5H_4Me)^-$
pdto	1,8-bis(2-pyridyl)-3,6-dithiaoctane
py	pyridine
TCNB	1,2,4,5-tetracyanobenzene
TCNE	tetracyanoethylene (ethenetetracarbonitrile)
TCNP	2,3,5,6-tetracyanopyrazine
TCNQ	7,7,8,8-tetracyano-*p*-quinodimethane (2,2′-(2,5-cyclohexadiene-1,4-diylidene)bispropanedinitrile)
TCNX	TCNE or TCNQ (collective designation)
TPP	*meso*-tetraphenylporphinato(2-)

1. SCOPE AND INTRODUCTION

Unsaturated polynitriles such as the prototypical electron acceptors tetracyanoethylene (TCNE) or 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) are fascinating compounds because of their extremely high electron affinities of ca. 3 eV [1] and their simple structure.



TCNE

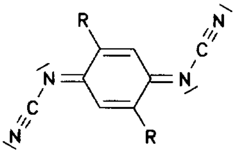


TCNQ

These two planar D_{2h}-symmetric molecules ("TCNX" for short) are reduced at about +0.2 V vs. SCE or Ag/AgCl in solution [2] with little reorganization energy [3]; the electrochemical potentials of the TCNX/TCNX$^{-\cdot}$ couples thus lie in a similar region as the ferrocenium/ferrocene pair (see Table 1, below) or typical Cu(II)/Cu(I) systems. Overall, the TCNX molecules can easily accommodate two extra electrons (eqn. (1)), and some tetracyanoarenoquinodimethanes can even form radical trianions [4].

$$\mathrm{TCNX} \overset{E_1}{\rightleftharpoons} \mathrm{TCNX}^{-\cdot} \overset{E_2}{\rightleftharpoons} \mathrm{TCNX}^{2-} \tag{1}$$

Since the electrons required by acceptors such as TCNE or TCNQ may be provided by (more or less) coordinating metal centres, the formation of various kinds of complex between the "non-innocent" [5] ligands TCNX and metal compounds has been investigated for quite some time. A previous review on transition metal compounds with TCNE and related "percyanocarbon" ligands was provided by Baddley [6] in 1968 and Fatiadi has recently summarized the reactions of TCNE with organometallic compounds [7]. Selected aspects of TCNX coordination chemistry were reviewed by Ittel and Ibers (TCNE [8]) and Endres (TCNQ [9]), while Hünig and Erk have described the properties of the related *N,N'*-dicyano-*p*-benzoquinonediimines (DCNQIs) as radical anion ligands in highly conducting salts with metal ions [10]. Main group metal species were predominantly studied in their electron transfer reactivity towards TCNE and related acceptors by Kochi [11] and in our group [12,13].



R_2–DCNQI

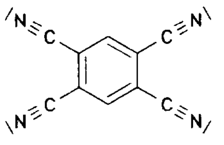
For a more general introduction to these unsaturated polynitriles, an excellent set of reviews is available by Fatiadi on TCNE, its properties and reactivity in organic chemistry [7,14], whereas the basic chemistry of TCNQ is summarized in the original article by Melby et al. [15].

The increasing attention given to the interaction of molecules such as TCNE or TCNQ with metal ions and complexes in recent years is due to a general interest in the study of electron transfer reactivity [11-13,16] and in the unusual physical properties displayed by such coordination compounds, especially in the solid state [9,10,17,18]. Highly anisotropic electrical conductivities [10,19-21], special magnetism [18,22-26] and unusual optical features [27,28] have been reported for such complexes.

The unsaturated polynitriles which were considered as ligands in this review include only such molecules (eqn. (2)) which have at least two π conjugated cyano substituents and which, starting from the neutral state, exhibit a first reduction potential more positive than -1.5 V vs. $Fc^{0/+}$, i.e. which can truly behave as non-innocent ligands.

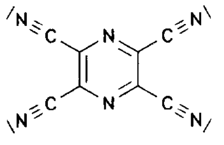
$$\pi(\text{-CN})_n,\ n \geqslant 2; \qquad E_{red} > -1.5 \text{ V vs. } Fc^{0/+} \tag{2}$$

Requirement (2) leaves mainly TCNE, TCNQ, DCNQI and derivatives [10], and the less intensely studied acceptor ligands 1,2,4,5-tetracyanobenzene (TCNB), tetracyanopyrazine (TCNP) and hexacyanobutadiene (HCBD [29(a),(c),(d)]) as subjects of this article.



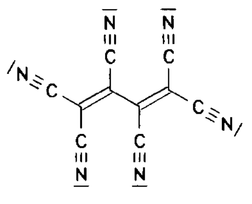
TCNB

(E_{red} -1.18 V vs $Fc^{0/+}$)



TCNP

(E_{red} -0.73 V vs $Fc^{0/+}$)



HCBD

While TCNE, TCNP and HCBD leave no possibility for further molecular modification, the TCNQ and, in particular, DCNQI systems have been studied in ring-substituted forms [9,10]. Weaker acceptors such as terephthalonitrile or fumaric dinitrile are not considered here, neither is 2,3-dichloro-5,6-dicyano-*p*-benzoquinone

(DDQ) which contains conjugated carbonyl π acceptor functions for possible metal coordination.

Another restriction concerns the types of complex treated in this article. The main focus is on "true" coordination compounds in which the metal centre(s) bind(s) strongly to the polynitrile ligand via the nitrile function(s) (Fig. 1, **I**) or via π coordination (Fig. 1, **II**). "Ion pairs" (**III**) [30–35] held together just by Coulombic forces between TCNX^{n-} and L$_n$M^{n+} and "charge transfer complexes" (**IV**) [26,36–42] with π-type interactions between TCNX$^{(n-)}$ and, for example, organometallic-substituted π systems [11,12,36], saturated polysilanes [37] or carbocyclic "decks" of metallocenes [38] but with no direct polynitrile-to-metal bonds will not be discussed in detail. Of course, the distinction in Fig. 1 is an arbitrary one with possible intermediate bonding arrangements. The emphasis on the *coordination* chemistry leaves structural aspects and the fundamental question of electron distribution as the main topics in this article. Accordingly, the reactivity (Sect. 4) and the potential applications in the materials field (Sect. 5) will be discussed rather briefly. Although many unusually rapid [27,43–46] reactions have been described, for instance between TCNE and metal compounds which lead to the formation of free TCNE$^{-\cdot}$ or its complexes [27,47–51], the full course and the product distributions of such reactions have not always been clear except for obvious electron transfer contributions (see

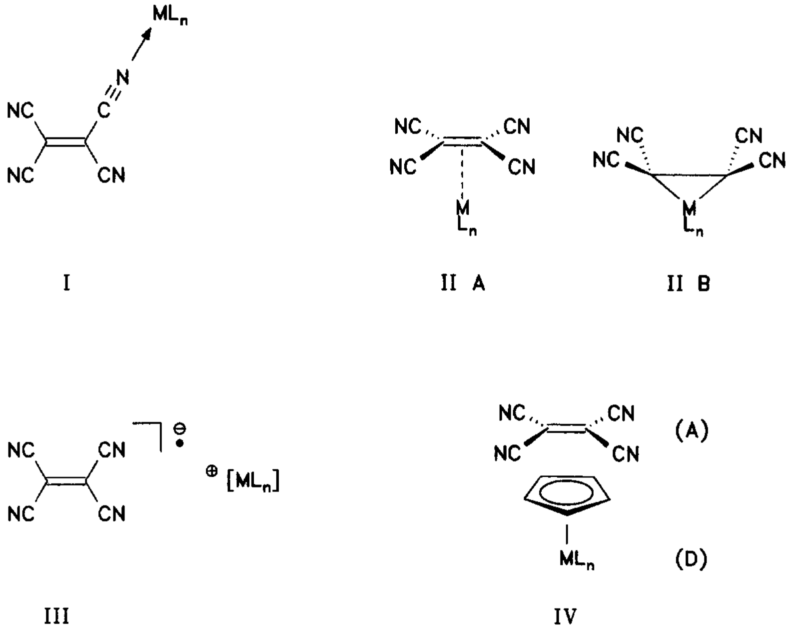


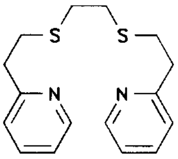
Fig. 1. Prototypical examples of metal interactions with polynitrile ligands (here: TCNE). Single nitrile N (σ) coordination (**I**); π complex (**IIA**, metallacyclopropane formulation **IIB**); ion pair arrangement (**III**); "charge transfer" complexation with π/π acceptor/donor interaction (**IV**).

Sect. 4.1). Due to the absence of stabilizing chelate effects, some very interesting coordination compounds of the TCNX ligands have remained too labile for isolation [50] or, if polymeric, very difficult to characterize, such as the non-crystalline room-temperature ferrimagnet $\mathrm{V(TCNE)}_x\cdot y\mathrm{CH_2Cl_2}$ [24].

2. LIGAND PROPERTIES

2.1 Polynitriles as stacking ligands

Polynitrile molecules such as TCNE, TCNQ, TCNB or TCNP are essentially planar [35,39] in the 0 and −1 oxidation states, which allows π/π interactions (→homo- or hetero-stacking [35,52,53]) even of (σ-)coordinated species such as (η^1-TCNE)Os(PPh$_3$)(η^2-S$_2$PMe$_2$) [54], (η^1-TCNE)Mn(CO)$_2$Cp [55] (Fig. 2), or (η^1-TCNQ)Cu(pdto) [56].



pdto

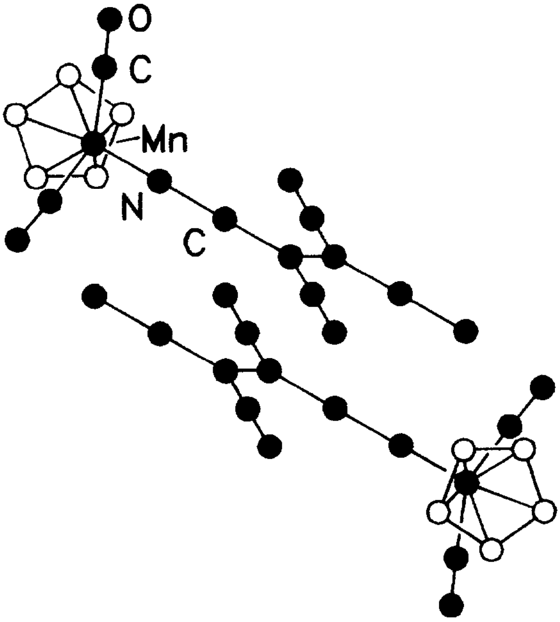
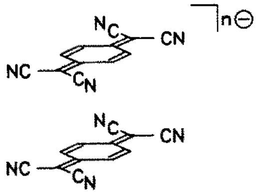
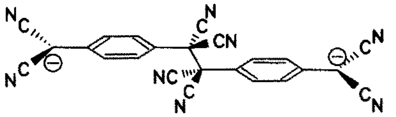


Fig. 2. π/π Dimerization of (η^1-TCNE)Mn(CO)$_2$(C$_5$H$_5$) in the solid (from ref. 55). Note the coincidence of the TCNE π plane and the mirror plane of Mn(CO)$_2$(C$_5$H$_5$) due to pπ/dπ bonding.

The larger π systems TCNQ and DCNQI are particularly susceptible to stacking [10,52,56,57] and dimerisation as in π/π bonded $(TCNQ_2)^{-/2-}$ [40,41,52] or σ/σ bonded $(TCNQ_2)^{2-}$ [58].





The weak binding of neutral metal complex fragments can thus result in the formation of solids with additional non-coordinated polynitrile molecules [38(d),59] such as *cis*-[(TCNB)Mo(CO)$_2$(dmpe)$_2$]·8TCNB [60] or (TCNE)Mo(CO)$_5$·10TCNE [61].

2.2 *Polynitriles as ambidentate ligands*

Unsaturated polynitriles are ambidentate ligands which can coordinate directly to metal centres via the olefinic or carbocyclic π system (η^2, perhaps [62] η^6 for TCNQ) or via the nitrile nitrogen lone pair(s) (Fig. 1, **I**, **II**). To a first approximation, "soft" metal centres prefer the π coordination whereas "hard" electrophiles are bonded rather in σ fashion via the nitrogen lone pairs of a cyano substituent [90]. However, the possibility of at least three available oxidation states (1) for these non-innocent ligands (see Scheme 1, below) creates a more complicated situation for the occurrence and interpretation of coordination preferences, as illustrated by the electron transfer-induced coordination change of (TCNE)W(CO)$_5$ (see Scheme 2) [63]. Other, more exotic binding modes of the nitrile group —C≡N such as the η^2 (side-on) coordination [64] have not yet been observed with the ligands described here.

2.3 *Polynitriles as bridging ligands*

The presence of four widely separated nitrile N coordination sites (Fig. 3) renders the compounds TCNX as potentially polydentate bridging ligands capable of binding up to four metal centres ($\mu_{\leqslant 4}$-TCNX); tetranuclear complexes of TCNE are indeed known (with Ru [65,66], Mn [27], V [67]), TCNQ, TCNB and TCNP (Ru [66]). The μ_4 coordination mode is also realized in solid state structures, e.g. of M(TCNQ), M = Cu, Ag [31].

The scale drawings in Fig. 3 not only illustrate the space available for the coordination of four rather bulky metal complex fragments, they also demonstrate that the sometimes claimed [68,69] chelation of metal centres by two adjacent or geminal (1,1-)nitrile nitrogen atoms is quite unlikely because this would have to involve an inconceivable degree of bending of the CCNM groups. Bridging of two

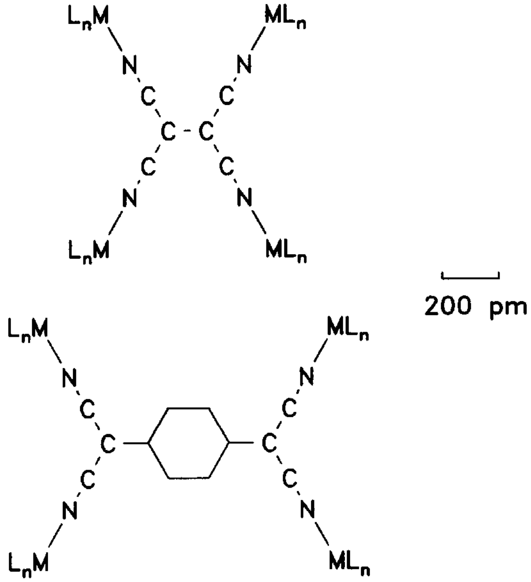


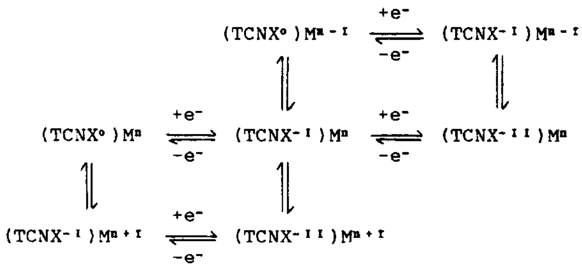
Fig. 3. Scale diagram of planar TCNE and TCNQ in tetracoordinated form (from standard bond parameters, see Table 1).

metal centres via double π coordination (sandwiching) has not yet been observed for TCNX ligands.

2.4 Polynitriles as non-innocent ligands

Unsaturated polynitriles such as TCNE or TCNQ can adopt various oxidation states (eqn. (1)) in their complexes with metals. The potentials of the corresponding ligand-centred redox processes in the complexes may be shifted to more negative or more positive values compared with the potentials of the free ligand, depending on the *net* charge transfer on complexation; contributions from the formation of the ligand-to-metal coordinative bond must be set off against those from metal-to-ligand π back-donation [70]. While complexes or ion pairs with main group metals are generally well defined with respect to oxidation states, the coordination compounds of TCNX molecules with redox-active transition metal compounds may be less clear-cut in terms of the electronic structure, i.e. with respect to the "best" assignment of oxidation states (Scheme 1). (In this article, the oxidation state is indicated by roman numerals whereas arabic superscripts refer to the actual charge.)

In the absence of direct information, e.g. from EPR [63] or NMR spectroscopy [71(a)], on the distribution of unpaired electrons, the structural [29(b),(c),39,52(a)], XPS [21,71(b),(c),72] and vibrational spectroscopic data [29(a),73] can indicate the "effective" oxidation state of metal-bound ligands such as TCNE and TCNQ. The presence of C≡N and C=C bonds and the absence of complicating functional groups



Scheme 1.

(including the absence of hydrogen atoms in TCNE, TCNP and HCBD!) often facilitate the interpretation of vibrational spectra, especially with regard to the symmetry and the assignment of oxidation states. Electron transfer equilibria of type (3) can occur, especially in complexes with metals such as nickel [74,75] or copper [71], which easily undergo ligand-dependent redox processes, e.g. Cu(II)/Cu(I) [21,76], at potentials close to that of the acceptor ligand.

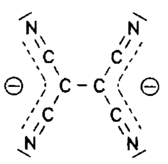
$$(\mathrm{TCNQ}^{-1})_2\mathrm{Cu}^{\mathrm{II}}\mathrm{L}_n \rightleftharpoons (\mathrm{TCNQ}^{-1/2})_2\mathrm{Cu}^{\mathrm{I}}\mathrm{L}_n \tag{3}$$

Such electron transfer equilibria, which are reminiscent of the situation in dioxolene (e.g. semiquinone) complexes [77], may play a role in the mechanism of solid state conductivity of, for example, copper/DCNQI compounds [10,71,78].

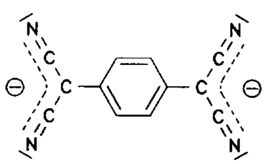
$$(\mathrm{DCNQI}^{-1})_2\mathrm{Cu}^{\mathrm{II}} \rightleftharpoons (\mathrm{DCNQI}^{-1/2})_2\mathrm{Cu}^{\mathrm{I}} \tag{4}$$

Eventually, the mixing of metal(s) and polynitrile π orbitals can become very extensive and render integer oxidation state assignments less useful. In such cases, Hückel-type MO calculations for discrete complexes [27] or band structure approaches are better suited to describe electronic structures [31,78]. In this article, we frequently use the oxidation numbers as given in the references, although their significance may be limited for the reasons cited above. Furthermore, oxidation numbers reflecting the charge distribution may not necessarily be directly useful for describing the magnetic behaviour which is affected, for example, by spin coupling (see below).

The electron pair formulae, e.g. for the neutral and dianionic forms of TCNE and TCNQ and the data from Table 1, illustrate the major geometry changes which were calculated and found experimentally for free and coordinated forms of the ligands in different oxidation states [29(b),35,39,52(a),79].



TCNE^{2-}



TCNQ^{2-}

TABLE 1

Structural and vibrational characteristics of coordinated TCNE (and TCNQ, in parentheses) in different oxidation states (from refs. 29(b), 35, 52(a), 79, 135, 141)

	Oxidation state of TCNX		
	0	-I	-II
Electrochemical potentials of the free ligands			
E^a	−0.28 (−0.25)	−1.45 (−0.97)	
Bond parameters^b			
$d(CN)^c$	113	114	116
$d(C{-}CN)^c$	144	142	140
$d(CC)^d$	134 (137)	137 (142)	148
α^e	0	<12	>45
Infrared data^f			
$\tilde{\nu}(CN)^c$	>2220	2110–2220	<2100^h
	>2170		<2180
$\tilde{\nu}(CC)^g$	>1490	≈1400	<1300

[a] Redox potentials from cyclic voltammetry in acetonitrile/0.1 M n-Bu_4NPF_6.

[b] Bond lengths in pm.

[c] Similar values for TCNE and TCNQ.

[d] Exocyclic bonds.

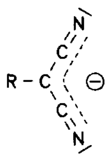
[e] Dihedral angle (deg) between $C(CN)_2$ moieties.

[f] Wavenumbers (cm^{-1}).

[g] Only TCNE considered.

[h] π-coordinated $TCNE^{-II}$ has $\tilde{\nu}(CN) > 2200\ cm^{-1}$ due to non-conjugated nitrile groups (see text).

For TCNE, the reduction results in the lengthening of the central C—C bond and in a tendency away from the co-planar structure, especially after addition of the second electron. For TCNQ, the reduction causes an "aromatization" in the six-membered ring [15,52(a)] and a lengthening of the exocyclic double bonds [52(a),79]. On electron addition to TCNX, the cyano groups become involved in a malonodinitrilato-type structure [15,27,66,80] with decreased C—N but increased C—C bond order.



malonodinitrilato anion

The lengthening of bonds resulting from decreasing bond order is also associated with low-energy shifts of corresponding vibrational frequencies, however, the nitrile stretching frequency depends not only on the oxidation state but also on the charge, on the π conjugation, and on the back-donating capability of the coordinated metal. It is thus important to note that the nitrile stretching frequencies of π-bonded TCNE^0 are *lower* than those of coordinated η^2-TCNE$^{-\text{II}}$ because of π back donation in the former (olefin) complexes (Fig. 1, **IIA**) and the metallacyclopropane formation with essentially non-conjugated nitrile groups in the latter (Fig. 1, **IIB**). Tables 1 and 2 contain some representative data.

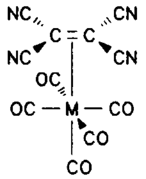
2.5 Interdependence of coordination and electron transfer

The neutral TCNX molecules are rather poor σ nucleophiles and their interaction with "normal" metal electrophiles such as Li$^+$ is quite weak in that form. In the (metal-)reduced states (-I, -II), however, these molecules become much more nucleophilic, forming more or less strongly bonded "ion pairs" with cations such as M$^+$ [10,30,31,35,81], $[\text{Cu(2,9-dmphen)}_2]^+$ [58], $[\text{M(bpy)}_3]^{2+}$ [33], $[(\text{PPh}_3)_2\text{Au}]^+$ [34] or metal clusters such as $[\text{Nb}_3(\mu\text{-Cl})_6(\text{C}_6\text{Me}_6)_3]^{2+}$ [40], which may be characterized structurally in the solid state or, for example, via EPR spectroscopy in solution; many such ion pairs dissociate in polar solvents. As very potent π acceptors, the polynitriles can also coordinate to low-valent metals via π back donation without full transfer of an electron in the ground state, as illustrated by the complexes $(\text{CO})_5\text{M}(\eta^2\text{-TCNE})$ (**1**), M = Cr, Mo, W [61,62,82–86].

TABLE 2

Representative vibrational data (cm^{-1}) of neutral η^1-and η^2-coordinated complexes of TCNE from infrared (IR) and resonance Raman (RR) studies

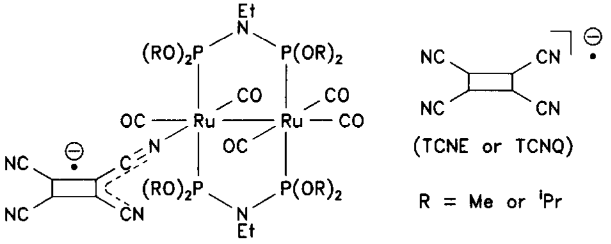
Complex		ν(CN)	ν(CC)	Ref.
$(\eta^2\text{-TCNE}^0)\text{W(CO)}_5$	IR:	2210 (vw) 2190 (s)	n.a.	62
	RR:	2223 2171	1491	86
$(\eta^2\text{-TCNE}^{-\text{II}})\text{Pt(PPh}_3)_2$	IR:	2220	n.a.	6
$(\eta^1\text{-TCNE}^{-\text{I}})\text{VBrCp}_2$	IR:	2215 (w) 2190 (s) 2155 (s) 2130 (m)	1410 (m)	67,90
$\{(\mu\text{-TCNE}^0)[\text{Cu(hfacac)}_2]\}_n$	IR:	2262 2252 2220	n.a.	139
$\{(\mu\text{-TCNE}^{-\text{I}})\text{Mn(TPP)}\}_n$	IR:	2192 (s) 2147 (m)	n.a.	25
	RR:	2195	1418	93
$(\mu\text{-TCNE}^{-\text{II}})[\text{Ir(CO)(PPh}_3)_2]_2$	IR:	2175 (s) 2098 (vs)	1256 (m)	29(a), (b)



M = Cr, Mo, W

1

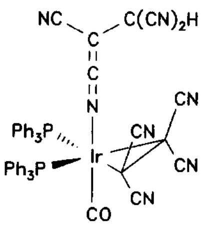
The occurrence of the reduction potentials of TCNX in the region of typical transition metal redox couples allows corresponding electron-transfer reactions to occur as inner-sphere or outer-sphere processes. Accordingly, reduced TCNX ligands can coordinate directly to metal compounds or form just weak ion pairs $(\mathrm{TCNX}^{n-})\cdots(\mathrm{L}_n\mathrm{M}^{n+})$ or π/π bonded charge transfer complexes $(\mathrm{TCNE}^{\delta-})$ $(\mathrm{L}_n\mathrm{M}^{\delta+})$ (Fig. 1, **III** and **IV**); different types of ligation can even be present in a single compound as discussed for $[(\eta^1\text{-TCNE}^{-\mathrm{I}})\mathrm{Fe}^{\mathrm{II}}(\mathrm{dppe})](\mathrm{TCNE}^{\cdot-})$ [50] and $\{(\mu\text{-TCNE}^{-\mathrm{II}})[\mathrm{Ti}^{\mathrm{IV}}(\mathrm{CO})\mathrm{Cp}_2]_2\}(\mathrm{TCNE}^{2-})$ [87] or, as recently established by EPR/ENDOR spectroscopy, for $[(\eta^1\text{-TCNX}^{-\mathrm{I}})\mathrm{Ru}^{\mathrm{I}}_2(\mathrm{CO})_5(\mathrm{L})_2](\mathrm{TCNX}^{\cdot-})$, $\mathrm{L}=\mu\text{-}(\mathrm{RO})_2\mathrm{PN}(\mathrm{Et})\mathrm{P}(\mathrm{OR})_2$ (**2**) [88]. A partly hydride-reduced compound $(\eta^2\text{-TCNE}^{-\mathrm{II}})[\eta^1\text{-NCC}(\mathrm{CN})\mathrm{C}(\mathrm{CN})_2\mathrm{H}]\mathrm{Ir}(\mathrm{CO})(\mathrm{PPh}_3)_2$ (**3**) was postulated based on infrared spectra [89].



(TCNE or TCNQ)

R = Me or ^{i}Pr

2a (TCNE)
2b (TCNQ)



3

In the absence of a crystal structure determination, EPR and IR or Raman vibrational spectroscopy were found suitable not only for determination of the effective oxidation state of the polynitrile ligands (cf. Tables 1 and 2) but also for establishing the symmetry and, therefore, the coordination mode by the number and intensity of bands [29(a),62,84,90,91].

2.6 Polynitriles as paramagnetic ligands

Transition metal complexes with stable anion radical ligands [92] such as $TCNX^{-\cdot}$ ($S=1/2$) can be interesting with respect to their magnetism, especially if the coordinated (or ion-paired) metal centres display some magnetism of their own. A variety of spin–spin coupling patterns was thus established for $(TCNE^{-\cdot})$ complexes of manganese [23,25,26,93–95] because low-valent manganese centres have an inherently small ligand field splitting (see Sect. 5.2).

3. SURVEY OF COMPLEXES

3.1 π Complexes (η^2; side-on C–C coordination)

The well-known [8,96] alternative between the olefin complex (Fig. 1, **IIA**) and metallacyclopropane formulation (Fig. 1, **IIB**) is nicely illustrated by complexes of TCNE. The contribution from the two resonance forms (Fig. 1, **II**) depends on the extent of metal-to-ligand electron transfer in the ground state.

Metallacyclopropanes involving strongly binding [97] η^2-$TCNE^{2-}$ as ligand are textbook cases [96], they have been structurally documented in several instances and were reviewed by Baddley in 1968 [6]. The common feature is the presence of a metal centre which has formally reduced TCNE to $TCNE^{-II}$ by changing from an electron rich d^n to the d^{n-2} state (oxidative addition [8,96–98]); a following reductive elimination can result in the net substitution of two negatively charged ligands [8].

$$Pt^{II}L_2XH + TCNE \rightarrow (TCNE^{-II})Pt^{IV}L_2XH \xrightarrow{-HX} (TCNE^{-II})Pt^{II}L_2 \tag{5}$$

where $L=PPh_3$, $X=$halide.

The most revealing structural features are the lengthening of the η^2 coordinated central C–C bond from typical 134 to about 148 pm and the corresponding tendency from sp^2 towards sp^3-type, i.e. tetrahedral carbon centres, illustrated by the back-bending of the cyanide groups (Fig. 1, **IIB**). The IR absorption wavenumbers $\tilde{\nu}_{CN}$ in such 2,2,3,3-tetracyanometallacyclopropanes are those of normal, non-conjugated cyanide substituents at ca. 2220 cm^{-1}.

Among the numerous obvious examples for such metallacyclopropane complexes of $TCNE^{-II}$ with d^0, d^2, d^6, and d^8 metal centres are $(TCNE)MoCp(PR_3)(CCH_2$-*tert*-Bu) [99], $(TCNE)Mo(CO)_2Cp(\eta^1$-$CH_3CNR)$ [100], $(TCNE)W(RCCR')(S_2CNR''_2)$ [44], $(TCNE)Fe(PR_3)(COR)Cp$ [101], (TCNE)-$Fe(CO)_2[P(OAr)_3]_2$ with trans CO groups [102], (TCNE)Fe-$(CO)[P(OMe)_3](\eta^4$-$C_4Ph_4)$ [48], $(TCNE)Fe(CO)_n$ $(CNR)_{4-n}$, $n=1$ or 2 [103], (TCNE)Fe(CO)$_2$(PPh$_3$)$_2$ [104] with trans CO groups, (TCNE)Ru(CO)$_4$ [105], [(TCNE)Co(CNAr)$_4$]$^+$ [49], (TCNE)Co(NO)(CNAr)$_2$ [106(b)], (TCNE)CoCp(PMe$_3$) [107], (TCNE)Rh(CO)Cp [108], (TCNE)Rh(C$_2$Ph)(PPh$_3$)(NCCH$_3$) [109], [(TCNE)Rh(CNR)$_{4-n}$(PPh$_3$)$_n$]$^+$, $n=0$, 1, 2 [106(a)], (TCNE)Rh(CNAr)$_2$(S$_2$CNR$_2$) [110], (TCNE)Ir(CO)(AsPh$_3$)$_2$Cl [111], (TCNE)Ir(CO)(PPh$_3$)$_2$(L), L = Br$^-$, C$_6$N$_4$H$^-$, CN$^-$ [87,112,113], (TCNE)Ni(Me$_2$NCH$_2$CH$_2$NMe$_2$) [75], (TCNE)Ni[Ph$_2$P(CH$_2$)$_4$PPh$_2$] [114], (TCNE)Pd(PPh$_3$)$_2$ [115(a)], (TCNE)Pd(diop) [115(b)], (TCNE)Pt(PPh$_3$)$_2$ [116], (TCNE)Pt(PPh$_3$)$_2$ClMe [98], (TCNE)Pt(η^3-C$_3$H$_5$)$_2$ [117], and reactive (TCNE)Au(PMe$_2$Ph)Me·THF [118].

Olefin-type complexes of (non-reduced) TCNE^0 are not very common. IR evidence suggests that (TCNE)Ni(bpy) [74] with π-accepting 2,2′-bipyridine (bpy) instead of the saturated tetramethylethylenediamine ligand [75] could belong to this category; furthermore, the NMR-detectable rotation of TCNE in isocyanide complexes of Co, Rh and Ni with TCNE [106,110] points to d^8 formulations involving **IIA** rather than to a rigid d^6 metal-containing structure **IIB**. Despite an early erroneous claim for the compound (TCNE)Mn(CO)$_2$Cp [82], only complexes **1** of TCNE with the pentacarbonyls M(CO)$_5$, M = Cr, Mo, W [82–86] and with pentakis-(arylisocyanide)chromium(0) [43] are clearly recognized to contain TCNE bound as an olefin. As is typical for M(CO)$_5$ complexes, the molybdenum compound is by far the most labile in the series of compounds **1**, crystallizing only with an excess of non-coordinated TCNE molecules as (TCNE)Mo(CO)$_5$·10TCNE [61]. Although an X-ray structure is not yet available for these compounds **1**, the infrared [62] and resonance Raman data [86] of the hydrogen-free organometallics (TCNE)M(CO)$_5$ prove unambiguously the η^2-coordination. Table 2 illustrates the characteristic vibrational spectroscopic differences between η^1- and η^2-coordinated TCNE, also in relation to the oxidation state. A very typical feature of η^2(C=C) coordination is the closeness of the two IR-detectable nitrile stretching frequencies [6,43,62,86].

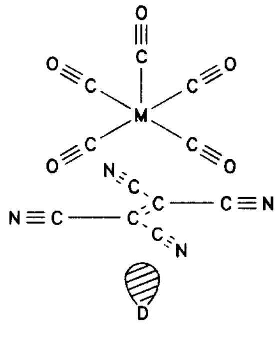
Several remarkable features are associated with the unusual situation that *non-reduced* TCNE forms π complexes with electron-rich d^6 metal centres as in the diamagnetic complexes (TCNE)M(CO)$_5$:

(a) The reduction potentials of the complexes **1** are very similar to those of the free ligand TCNE [84]. This result not only renders the complexes as potent π acceptors [85], like TCNE itself, it also indicates that the coordinative olefin-to-metal π electron donation is compensated by the charge shift from d(metal)-to-π^*(TCNE) back donation [84]. The slightly more negative reduction potential of the chromium analogue points to better back donation because of a closer distance and hence better orbital overlap.

(b) A low-energy symmetry-allowed metal-to-ligand charge transfer (MLCT) transition, approximated as

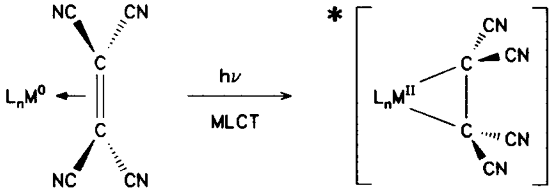
$$\mathrm{M^0\ (TCNE^0)} \rightarrow {}^*[\mathrm{M^{+1}(TCNE^{-1})}]$$

is possible from the ground state [84]. Such long-wavelength MLCT bands in the visible ($\lambda > 600$ nm) are unprecedented for normal olefin complexes [119]. Due to their strong π acceptor character, the complexes $(CO)_5M(TCNE)$ display a pronounced and peculiar solvatochromism [85]. The "free" TCNE side in the complex can act as a π accepting entity (as in free TCNE), interacting strongly with n or π electron-donating solvent molecules such as ethers and methylbenzenes. The curious result of such a three-component system metal/π acceptor/donor is that the nonpolar mesitylene solvent causes a much more pronounced hypsochromic shift of the MLCT band than the very polar but poorly electron donating nitrobenzene [85].

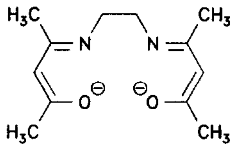


(n or π donor)

(c) A resonance Raman study of $(CO)_5M(TCNE)$, M = Cr, W [86], has not only confirmed the olefin (η^2) coordination and the non-reduced character of bound TCNE; it has also illustrated the higher degree of back donation in the chromium complex and the corresponding tendency from the olefin (**IIA**) to the metallacyclopropane formulation (**IIB**) on MLCT excitation. In particular, low-energy three-membered ring distortion and polycyanide rocking and scissoring modes showed a resonance Raman enhancement on excitation within the MLCT bands [86].



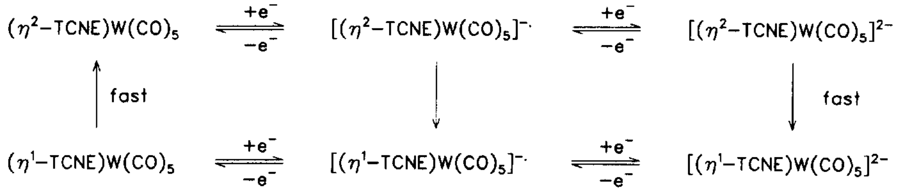
Conventional metal π complexes of TCNQ (and of TCNB or other such ligands) are quite rare and have not yet been structurally characterized [62,120]. Tightly bound π complexes with metal—carbon distances of less than 250 pm [112,116] must be distinguished from ion pairs forming mixed stacks with $d(M-C) > 300$ pm [53]. For instance, the reaction of Co(acacen) with TCNQ in pyridine [121] yields a complex containing dimerized reduced TCNQ, i.e. a well-known product of preferentially self-stacking $TCNQ^{-\cdot}$ [52], while TCNE gives a dimer with μ,η^2 $(N^{1,3})$-TCNE bridging two Co(acacen)py fragments [91].



acacen

The more extended π system of TCNQ relative to TCNE clearly favours π/π interactions and disfavours electrostatic metal/ligand binding due to a more delocalized negative charge in the acceptor π system [84,122]. Nevertheless, the analogues of complexes **1**, i.e. the highly labile (TCNQ)M(CO)$_5$, M = W, Cr, compounds could be prepared and studied spectroscopically [62,84]; infrared vibrational data suggest a symmetrical π coordination despite the fact that the exocyclic double bonds are better suited for π back donation [84] than the six-membered cyclohexadiene ring.

While π complexes of TCNE are established with the dianionic and neutral form of that ligand, it is significant that no such stable complexes have been obtained in the case of the radical state. A recent cyclovoltammetric study has shown that the apparently simple one-electron reduction of the complex (TCNE)W(CO)$_5$ is followed by a relatively rapid rearrangement to the spectroscopically well detectable nitrile N-coordinated form of the anion radical complex, a process which is fully reversible albeit with some hysteresis [63]. The diminished π-accepting capability of the anion radical state with the half-occupied orbital $(\pi^*)^1$ and the delocalization of negative charge to the nitrile nitrogen centres in that essentially planar (-I) form [35,39] are responsible for this unusual electron transfer-induced rearrangement (Scheme 2).



Scheme 2.

A similar rearrangement $\eta^2\text{-TCNE}^{-1} \rightarrow \eta^1(\text{N})\text{-TCNE}^{-1}$ in the (TCNE)M(CO)$_3$(L), complexes L = α-diimines, was reported recently on the basis of vibrational spectra [123].

The metal coordination and electrochemistry of π acceptor olefins have attracted renewed attention recently in connection with fullerenes such as C_{60} which has $E_{\text{red}} = -0.86$ V vs. $\text{Fc}^{0/+}$ [124].

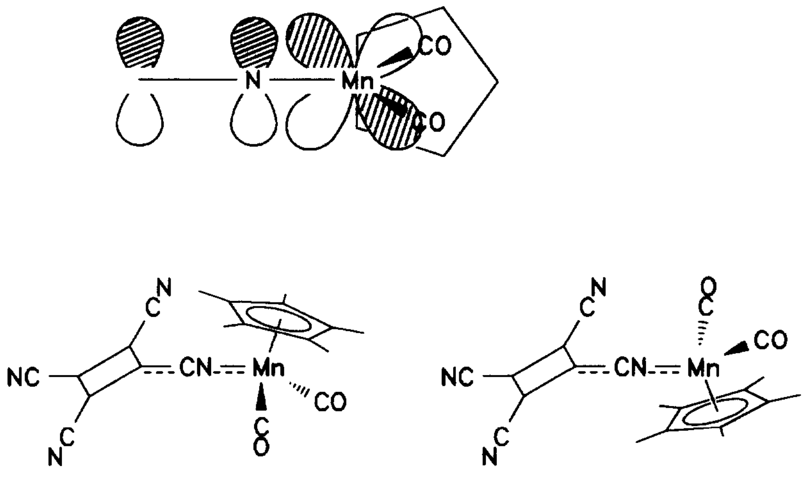
3.2 Mononuclear σ complexes (η^1; end-on N coordination)

The explanation given above to rationalize the electron transfer-induced coordination change (Scheme 2) is probably responsible for the fact that most hitherto isolated complexes of η^1(N)-TCNE contain the (-I) state of the ligand; other states of TCNE in corresponding complexes may, however, be accessible electrochemically or via chemical redox reactions [88].

The paramagnetic species $TCNE^{-\cdot}$ may be connected to a diamagnetic metal centre in neutral, negatively or positively charged anion radical complexes such as (η^1-$TCNE^{-I}$)$Mn^I(CO)_5$ [125], [(η^1-$TCNE^{-I}$) $W^0(CO)_5]^{-\cdot}$ [63] or [(η^1-$TCNE^{-I}$)-$Ru_2(CO)_5(L)_2]^+$, L = μ-$(RO)_2PN(Et)P(OR)_2$ (**2**) [88]. However, $TCNE^{-I}$ can also be bound to an odd-electron metal system. In cases such as (η^1-TCNE)VCp_2Hal, Hal = Cl, Br, I [90], or (η^1-TCNE)Co(L)(MeCp), L = CO, PR_3, py [126], the obvious (IR, X-ray structure) *charge distribution* according to the formulation $TCNE^{-I}/V^{IV}$ or $TCNE^{-I}/Co^{II}$ does not result in full-scale ($S = 1$) paramagnetism because of intermediate [126] or even strong spin-pairing ($S = 0$) [90,127]. In the complexes (η^1-$TCNE^{-I}$)$Mn^{II}(CO)_2(C_5R_5)$ [27,55,84] (Fig. 2) with XPS-detectable Mn^{II} [72] there is an additional metal-based paramagnetism arising from a small ligand field splitting which is *not* specifically affected by the presence of the TCNE ligand [95]. The isolated and studied complexes of η^1-$TCNE^{-I}$ are (TCNE)VCp_2Hal, Hal = Cl, Br, I [67,90], (TCNE)$Cr(CO)_2(C_6Me_6)$ [45,62,84], (TCNE)$Mn(CO)_2(C_5R_5)$, R = H, Me [27,55,62,72,82,84,95], (TCNE)$Mn(PR_3)Hal_2$ [94], (TCNE)$Mn(CO)_2(L)(SnPh_3)$, L = *tert*-BuN=CH–CH=N-*tert*-Bu [123], [(TCNE)$Ru(NH_3)_5](PF_6)_2$ [65,66], (TCNE)Os(CO)$(PR_3)_2$HCl, R = cyclohexyl [128,129], (TCNE)$Os(PPh_3)(\eta^2$-$S_2PR_2)_2$, R = Me, Ph [54], (TCNE)Co(L)(MeCp), L = CO, PR_3, py [126], (TCNE)SnR_3 [138] and [(TCNE)$Ru_2(CO)_5(L)_2$](TCNE), L = μ-$(RO)_2PN(Et)P(OR)_2$ (**2a**) [88].

The latter complex contains $TCNE^{-I}$ both in the inner (η^1) and in the outer coordination sphere (i.e. as dissociable counterion), it is also the first well-characterized complex containing a TCNE-coordinated metal dimer. EPR spectroscopy confirmed the presence of free and η^1(N)-coordinated $TCNE^{-\cdot}$ in these stable complexes **2a** [88], the EPR technique was also used to detect other, not isolated η^1(N)-coordinated $TCNE^{-\cdot}$ complexes such as [(η^1-$TCNE^{-I}$)$W^0(CO)_5]^{-\cdot}$ [63] (cf. Scheme 2) or (η^1-$TCNE^{-I}$)(ML_n), ^+ML_n = $^+M^{II}(CO)_3Cp$ (M = Cr, Mo), $^+Mn^I(CO)_5$, $^+Fe^{II}(CO)_2Cp$ and $^+Sn^{IV}(C_4H_9)_3$ [125,131]. Three different ^{14}N hyperfine coupling constants are generally found [63,88,125,131] for η^1-coordinated $TCNE^{-I}$ because of the low symmetry and the degeneracy of two splittings [63].

The information from available crystal structure determinations [54,55,90] shows that the conformation between the π plane of $TCNE^{(n-)}$ and the η^1(N)-coordinated metal complex fragment is often crucial because it ensures dπ/pπ overlap (and spin pairing) [27,127] (Figs. 2 and 4). Such structural requirements can even be predicted [84] on the basis of available MO schemes [132], among the most obvious examples being the compounds (TCNE)$Mn(CO)_2(C_5R_5)$ (**4**) in which the mirror plane of the organometallic fragment and the TCNE π plane have to coincide (Figs. 2 and 4) [55,84] in order to allow full dπ/pπ orbital overlap. The restricted rotation around metal-to-ligand bonds with considerable π contributions may thus cause orientational isomerism [27,133] in the case of less symmetrical complex fragments at the nitrile coordination sites (Fig. 4).



syn anti

4

Fig. 4. Orientational isomerism in η^1-TCNX complexes resulting from pπ/dπ bonding with restricted rotation around the M–N bond (example from Fig. 2).

While EPR and IR vibrational spectroscopy can confirm the low symmetry of η^1-coordinated TCNE via the large number of EPR hyperfine lines [63,88,125,131] or IR absorption bands (4 ν_{CN}, 1 $\nu_{C=C}$) [62,90], the (-I) oxidation state of the ligand is evident from the shifts of vibrational absorptions (Tables 1 and 2) and from the appearance of a typical ($TCNE^{-I}$)-related absorption around 400 nm [39,84,88,124]. In many instances, the formation of an inert bond between the metal and one nitrile nitrogen centre of $TCNE^{-\cdot}$ requires a certain degree of π back bonding which not only places some restrictions on the conformation (Fig. 4) but also causes a cathodic shift of the reduction potential [84]. The reduction of such complexes, formulated [12,13,84] as

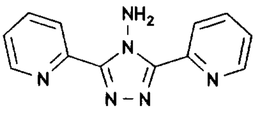
$$(TCNE^{-I})(L_nM^n) + e^- \rightleftharpoons (TCNE^{-II})(L_nM^n) \qquad (6)$$

often occurs at more negative potentials than the reduction

$$TCNE + e^- \rightleftharpoons TCNE^{-\cdot} \qquad (7)$$

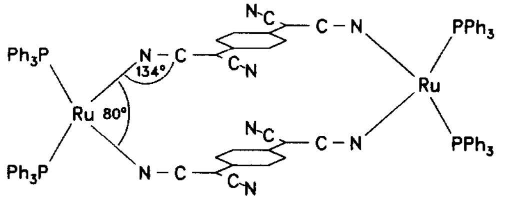
simply because there are different redox couples of TCNE involved (eqn. (1)). An exception among the complexes is again the diruthenium(I) system (**2**) [88] which, for stability, relies on the well-known inertness of the Ru–N (nitrile) bond [80,134] and not on strong π back donation from the metal.

Although there are more reported cases of nitrile-coordinated complexes with $TCNQ^{n-}$ than of metal-to-ligand π-bonded compounds, the propensity towards π/π stacking interactions and the potentially bridging function of $TCNQ^{n-}$ result in various kinds of intermolecular interactions. Of the structurally documented examples, (η^1-TCNQ^{-1})Cu^{I}(pdto) [56] and (η^1-TCNQ^{-1})$_2$Cu^{II}(abpt) [135] show stacking of η^1(N)-coordinated TCNQ^{-1}.



abpt

The molecular complex (TCNQ^{-1})$_2$Cu^{II}(abpt) [135] contains the rare example of a discrete metal centre coordinating to more than one polynitrile; an apparently polymeric complex (TCNE)$_3$Ru(PPh$_3$)$_2$ [136] and the compounds (TCNQ)$_2$SnX$_2$, X = Me, Cl, [68(b),(c)] and (TCNE)$_2$Ni(dmpae)$_2$ [130] were also reported. In many cases, the polydentate nature of TCNX leads to coordination oligomerization or polymerization if metal complexes with more than one open coordination site are available. For instance, (TCNQ)Ru(PPh$_3$)$_2$ exists as a diamagnetic dimer **5** with trans-1,2-bridging and additionally stacking μ-TCNQ^{-1} and magnetically coupled Ru(I) centres in the solid state [137]; in solution, this compound dissociates as evident from the typical vibrationally structured absorption spectrum of free TCNQ$^{-\cdot}$ with maxima at 842 and 395 nm [15].



5

In a related case, the dissociation of (η^1-TCNQ^{-1})Mn^{II}(CO)$_2$Cp* into free TCNQ$^{-\cdot}$ and a low-spin Mn^{II} species has been observed by EPR in polar solvents [84]; other apparently molecular complexes of η^1-TCNQ^{-n} include [(TCNQ^{-II})Ni^{III}(bdpa)]$^+$ [130], [(TCNQ^{-II})Sn^{IV}X$_3$]$^{-\cdot}$ [138], (TCNQ^{-1})Sn^{IV}X$_3$ and (TCNQ^{-1})$_2$Sn^{IV}X$_2$, X = Me, Cl [68(b),(c),138], (TCNQ^{-1})Re^{I}(CO)$_5$ [139], (TCNQ^{-1})Au(PPh$_3$)$_2$ [140] and [(TCNQ^{-1})Ru$^{I}_2$(CO)$_5$(L)$_2$]$^+$ (TCNQ$^{-\cdot}$) (**2b**) [88]. The external "free" TCNQ anion radical can be exchanged in **2b** with diamagnetic tetraphenylborate BPh$_4$, which greatly facilitates the interpretation of IR, UV/Vis and EPR/ENDOR spectra [88]. In analogy to the results for complexes with η^1-coordinated TCNE$^{-\cdot}$, the spectroscopic methods show similar effects for **2b** with regard to symmetry and oxidation state (IR), electronic transitions to low-lying excited states (UV/Vis/NIR) and spin distribution (EPR) [88].

Molecular metal complexes of η^1-coordinating DCNQI ligands are not well known, presumably because the terminal nitrogen atom of the cyanimido group is even less basic than a nitrile nitrogen centre. Vibrational infrared and electronic absorption spectra of very labile (2,5-DMDCNQI)Mn$(CO)_2$Cp* are similar to those of corresponding complexes of TCNE and TCNQ [84].

3.3 Polynuclear σ complexes (μ_n)

The presence of two (DCNQI), four (TCNX, TCNB, TCNP) or even six nitrile nitrogen coordination sites (HCBD, hexacyanobenzene) which are conjugatively coupled but rather far apart from each other (see Fig. 3) should allow the coordination of more than one metal complex fragment. The bridging capability of ligands such as TCNE in molecular coordination compounds was recognized by Crumbliss and Basolo [91] who studied dinuclear complexes of Co(acacen)(py) with TCNE and were immediately drawn to the question of isomerism (Fig. 5) in dinuclear complexes (1,1-, *cis*-1,2- and *trans*-1,2-coordination [27,29(a),133]).

According to structurally documented examples with TCNE [141,142] and TCNQ [137,143,144], it is often assumed that the trans-1,2 structure is favoured for steric reasons; this centrosymmetric structure can be inferred from IR vibrational spectroscopy [27,133] and has recently been found in linear chain coordination polymers involving μ-TCNE (**6**) [141] and μ-TCNE$^{-\cdot}$ (**7**) [26], in a bis-dinuclear complex of μ-TCNQ^{-1} (**8**) [143] and in cyclically dimeric complexes (**5**) [137] and ion pairs **9** [144] involving π/π interacting TCNQ$^{-\cdot}$.

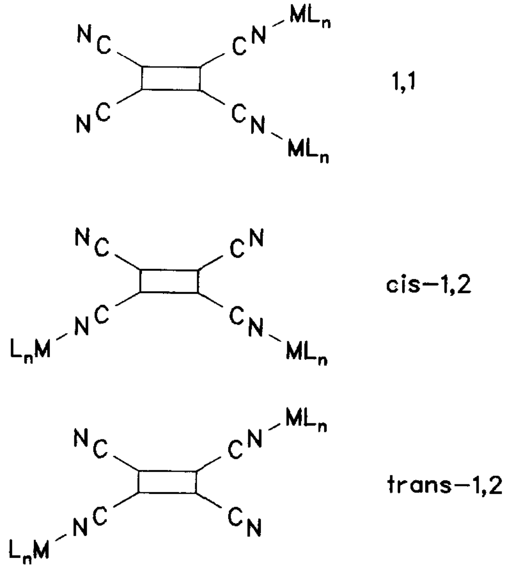
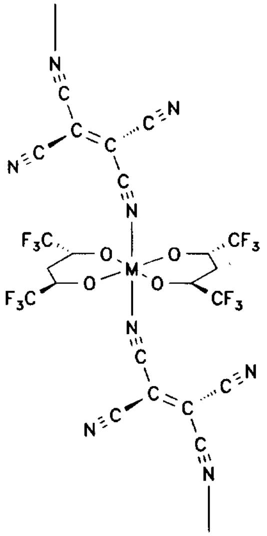
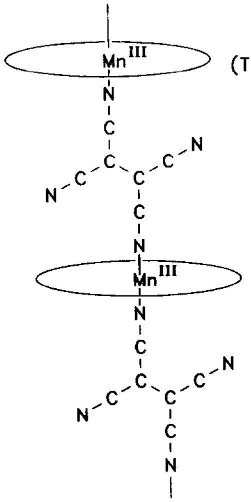


Fig. 5. Positional isomerism in dinuclear complexes of tetranitrile acceptor ligands (TCNE, TCNQ, TCNB, TCNP).



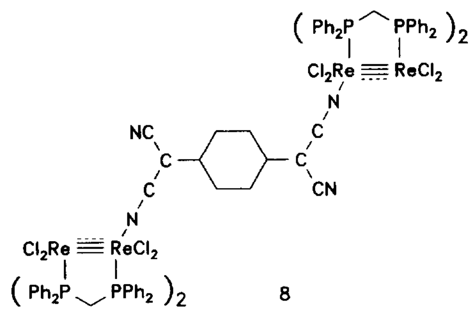
M = Cu, Co

6

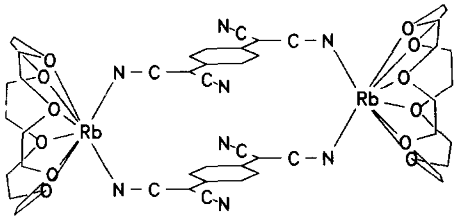


(TPP = meso-tetraphenylporphinato(2−))

7

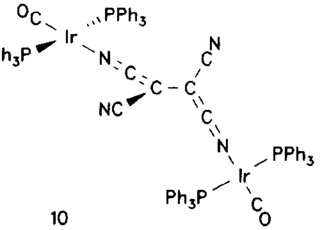


8



9

Beck et al. have proposed cis-1,2 coordination for (μ-TCNE^{-II})-[Ir^I(CO)(PR$_3$)$_2$]$_2$ (**10**) on the grounds of a high dipole moment and an IR absorption band attributed to the stretching of the central C—C bond of TCNE^{-II} [29(a)]; similar cis-1,2 structures were discussed for {(μ-TCNX^{-II})[Ni^{II}(bdpa)]$_2$}$^{2+}$, for the cyclically formulated complex {(μ-TCNQ^{-II})$_2$[Ni^{III}(bdpa)]$_2$}$^{2+}$ [130] and for {(μ-TCNE^{-II})[Ti^{IV}(CO)Cp$_2$]$_2$}(TCNE^{2-}) [87]. As the dinegative state of TCNX involves the connection of malonodinitrilato moieties via C—C single bonds with low activation barriers towards rotation, the cis/trans distinction may become irrelevant; in fact, a recent structure analysis of **10** has shown a dihedral angle between the C(CN)$_2$ groups of about 67° [29(b)].



10

Discrete dinuclear TCNE complexes with presumably trans-1,2 coordinated metals include compounds of $^+$Re(CO)$_5$ [139], Ru(CO)(PR$_3$)$_2$Cl$_2$, R = cyclohexyl [128], Os(CO)(PR$_3$)$_2$HCl, R = cyclohexyl [128] and isopropyl [129], Mn(CO)$_2$Cp* [27] and the structurally characterized {(μ-TCNE)[Cu(PPh$_3$)$_2$][Cu(CN)(PPh$_3$)$_2$]}$_n$ [142]. While Crumbliss and Basolo have reported a solvent dependence for the formation of the two isomers of (μ-TCNE)[Co(acacen)py]$_2$ [91], all three possible constitutional isomers from Fig. 5 were apparently obtained in the case of the complexes (μ-TCNE)[Ru(PPh$_3$)Cp(cyclo-C=CPhC(CF$_3$)$_2$C(CN)$_2$)] [133]. The TCNB ligand also seems to show this kind of isomerism of dinuclear complexes [133].

No positional isomerism exists for the tri- and tetranuclear complexes of TCNX ligands which are known for compounds with [Ru(NH$_3$)$_5$]$^{n+}$ (μ_4-TCNE,TCNQ,TCNB,TCNP) [65,66], [Re(CO)$_5$]$^+$ (μ_3-TCNQ) [139], Mn(CO)$_2$Cp* (μ_3-TCNE, μ_4-TCNE,TCNQ) [27], and VCp$_2$Br (μ_4-TCNE) [67]. The $\mu_4(\eta^1:\eta^1:\eta^1:\eta^1)$ coordination mode is also realized in solid state structures, e.g. of (TCNQ)Ag with four-coordinate metal [31]; similarly, DCNQIs display their coordinative saturation in solid state compounds, e.g. with copper [10,19,20]. In general, metal complex fragments with two or more open coordination sites may eventually form coordination polymers with μ-TCNX$^{(n-)}$ such as [(TCNE)Co(acacen)]$_n$ [91], [(TCNX)SnL$_m$]$_n$ [68(b),(c),138], [(TCNE)Cu]$_n$ [142(a)], [(TCNQ)(RuCp*)$_2$]$^{2+}$ [142(b)] or the ferrimagnetic V(TCNE)$_x$·yCH$_2$Cl$_2$ [24] and possibly related compounds [120]; coordination polymers involving trans-1,2 coordinating μ-TCNE (**6**) and μ-TCNE$^{-\cdot}$ (**7**) were characterized by structure analysis [26,141].

As in the mononuclear nitrile coordinated complexes, the oxidation states of bridging TCNX ligands in the discrete di-, tri- and tetranuclear complexes [27,29(a),(b),87,137] were established to be (-I) or lower in most cases, based on the IR vibrational spectra. In fact, the mere ability of such unsaturated polynitriles to form inert bonds with more than one metal centre can be attributed to the increased nucleophilicity of the reduced form(s) [27]. Exceptions are the coordination polymers [(μ-TCNE)M(hfacac)$_2$]$_n$, M = Cu, Co (**6**) which were produced in gas-phase reactions [141] and the complexes {(μ-TCNE)[Re(CO)$_5$]$_2$}$^{2+}$ and {(μ_3-TCNQ)[Re(CO)$_5$]$_3$}$^{3+}$ [139] which contain non-reducing but nitrile-affine pentacarbonylrhenium(I).

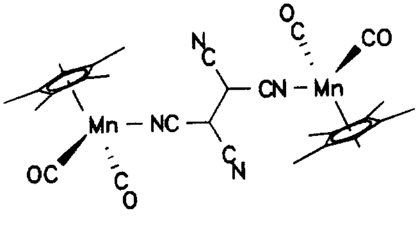
The electronic structure of most molecular dimers can thus be described by the resonance forms (eqn. (8)). The alternatives involve either neutral [91] or dianionic TCNX bridging of two strongly coupled metal species, or the connection of two formally mixed-valent metal centres by TCNX^{-I} [27]. Assuming a TCNX^{-II} ligand, the coupled metals can be even-electron species such as $^{+}$Co^{III}(acacen) [91]) or odd-electron centres such as $^{+}$Mn^{II}(CO)$_2$(C$_5$R$_5$) [27].

$$\begin{array}{ccc}(L_nM^m)(\mu\text{-TCNX})(M^mL_n) & \leftrightarrow & (L_nM^{m+I})(\mu\text{-TCNX}^{-I})(M^mL_n) \\ & & \updownarrow \\ & & (L_nM^{m+I})(\mu\text{-TCNX}^{-II})(M^{m+I}L_n)\end{array} \qquad (8)$$

The alternatives in eqn. (8) suggest that, due to considerable electron transfer upon complex formation, such compounds can serve as ground-state models for charge-transfer excited states of conventional dinuclear complexes between metal donors and π acceptors [27].

The anodic, i.e. "normal" shifts for the potentials of reversible reduction upon coordination of the second, third and fourth metal complex fragment confirm the non-electron transfer character of the second coordination in the cases of Mn(CO)$_2$Cp* [27] and [Ru(NH$_3$)$_5$]$^{n+}$ [66]. Accordingly, the coordination of additional metal complex fragments is often slower [27] than the electron transfer-catalyzed [46] reaction (see Scheme 3) leading to the mononuclear complexes. Strong metal-to-TCNE π bonding may eventually result in a delocalized situation best described within a Hückel MO formalism as depicted in Fig. 6, including the metal(s) as dπ centres [27]; indeed, both the delocalized (Fig. 6) and the localized model (Scheme 3) can account for the appearance of two intense long-wavelength charge transfer bands, e.g. in the compound (TCNE)[Mn(CO)$_2$Cp*]$_2$ (**11**) [27].

Tetranuclear complexes of the TCNX ligands with Mn(CO)$_2$Cp* and



11

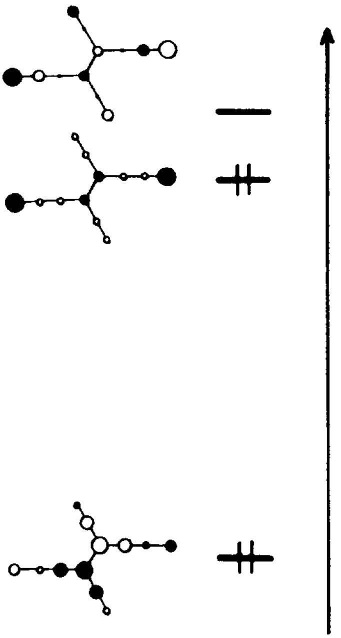
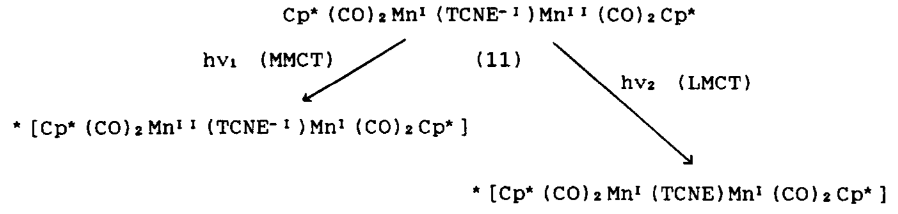
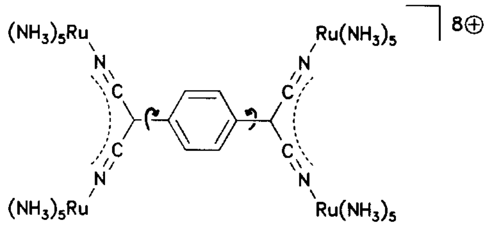


Fig. 6. Hückel MO diagrams for the frontier orbitals of (*trans*-μ-TCNE) $[Mn(CO)_2(C_5R_5)]_2$: metal-based LUMO and HOMO, TCNE-based SHOMO.



Scheme 3.

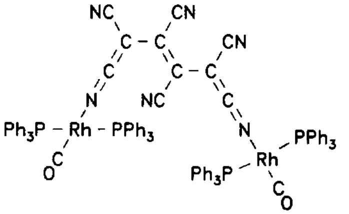
$[Ru(NH_3)_5]^{n+}$ such as **12** exhibit highly symmetrical structures, as deduced both from IR vibrational spectroscopy and from analysis of the optical spectra which are distinguished by a very intense long-wavelength absorption ($\varepsilon > 50\,000$ M^{-1} cm^{-1}) in the near infrared region [27,66]. Neither the stepwise one-electron oxidation of $\{(\mu_4\text{-TCNE})[Ru(NH_3)_5]^4\}^{(8+)\text{–}>(12+)}$ nor the virtual insensitivity reported [65] for the corresponding absorption spectra could be reproduced [66]. Instead, two-electron oxidation processes were observed for complexes $\{(\mu_4\text{-TCNX})[Ru(NH_3)_5]^4\}^{(8+)\text{–}>(10+)}$ [66] which indicate a rather weak electrochemical interaction between two mixed-valent Ru^{II}/Ru^{III}/malonodinitrilato [80] moieties, a view which is supported by magnetic susceptibility measurements [66].



12

In addition to the configurational isomerism for dinuclear complexes (Fig. 5), there is the previously mentioned possibility of orientational isomerism [27,133] because of the metal/nitrile π bonding (Fig. 4). Several such combinations can be possible in polynuclear complexes [27]; however, there are no structural analyses available yet regarding this question.

Nuclearities higher than four are possible in complexes of hexacyano-1,3-butadiene (HCBD) [29(a),(c),(d)] or the hitherto less studied hexacyanobenzene, but only symmetrically dinuclear complexes with $M(CO)(PPh_3)_2$, M = Rh, Ir, were described in connection with the dianionic HCBD ligand [29]. The structural characterization of $(HCBD^{-II})[Rh(CO)(PPh_3)_2]_2$, **13**, revealed a non-planar arrangement with a keteneiminato type of coordination to two peripheral nitrile groups [29(c)]; in contrast to the (K^+) ion-paired $HCBD^{2-}$ dianion [29(d)] the dirhodium(I) complex **13** shows a trans configuration of the central C=C bond [29(c)].



13

Table 3 summarizes some representative examples of TCNX complexes, illustrating the variety that results from (a) different oxidation states, (b) different coordination modes, and (c) different nuclearities.

4. REACTIVITY

4.1 Formation of complexes

We have already mentioned that, in most instances, the formation of TCNX complexes involves electron transfer steps. Evidence comes from the frequent occurrence of free or coordinated $TCNX^{-I}$ during the reaction or as a side-product

TABLE 3

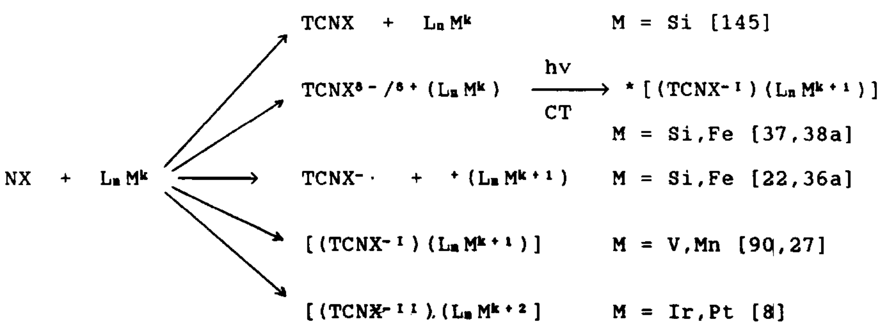
Well-established types of TCNX complexes as distinguished by nuclearity, coordination mode and approximate oxidation state of the ligand

Coordination mode	Example	Comments	Ref.
η^2-TCNX^0	(TCNE)W(CO)$_5$ (**1**)		62,82–86
η^2-TCNX^{-I}	[(TCNE)W(CO)$_5$]$^-$	Rapidly rearranging $\eta^2 \rightarrow \eta^1$	63
η^2-TCNX^{-II}	(TCNE)Pt(PPh$_3$)$_2$		6,116
η^1-TCNX^0	No established example		
η^1-TCNX^{-I}	(TCNE)VBrCp$_2$	Diamagnetic	90
	(TCNE)Mn(CO)$_5$	Ligand-based paramagnetism	125
	(TCNE)Mn(CO)$_2$Cp (**4**)	Metal-based paramagnetism	95
		π/π dimerization in solid	55
	[(TCNX)Ru$_2$(CO)$_5$(LL)$_2$]$^+$ (**2**)	External TCNX$^{-\cdot}$ as counterion	88
	(TCNQ)$_2$Cu(abpt)$_2$	Two η^1-TCNQ^{-I} ligands bound to one metal centre	135
η^1-TCNX^{-II}	No established example		
μ-TCNX^0	{(TCNE)[Re(CO)$_5$]$_2$}$^{2+}$		139
	[(TCNE)Cu(hfacac)$_2$]$_n$ (**6**)	Coordination polymer	141
μ-TCNX^{-I}	(TCNE)[Mn(CO)$_2$Cp*]$_2$ (**11**)		27
	(TCNQ)[Re$_2$Cl$_4$(dppm)$_2$]$_2$ (**8**)	Bridged Re≡Re units	143
	[(TCNQ)Rb(18-crown-6)]$_2$ (**9**)	π/π dimeric ion-pair	144
	[(TCNE)Mn(TPP)]$_n$ (**7**)	Coordination polymer, ferromagnetic coupling	25
μ-TCNX^{-II}	(TCNE)[Ir(CO)(PPh$_3$)$_2$]$_2$ (**10**)	Non-planar TCNE^{-II}	29(a), (b)
μ_3-TCNX^0	{(TCNQ)[Re(CO)$_5$]$_3$}$^{3+}$		139
μ_3-TCNX^{-I}	(TCNE)[Mn(CO)$_2$Cp*]$_3$		27
μ_4-TCNX^{-I}	(TCNX)[Mn(CO)$_2$Cp*]$_4$	Paramagnetic	27,95
	[(TCNQ)Ag]$_n$	Solid	31
μ_4-TCNX^{-II}	{(TCNX)[Ru(NH$_3$)$_5$]$_4$}$^{8+}$	Pairs of weakly coupled mixed-valent dimers	65,66

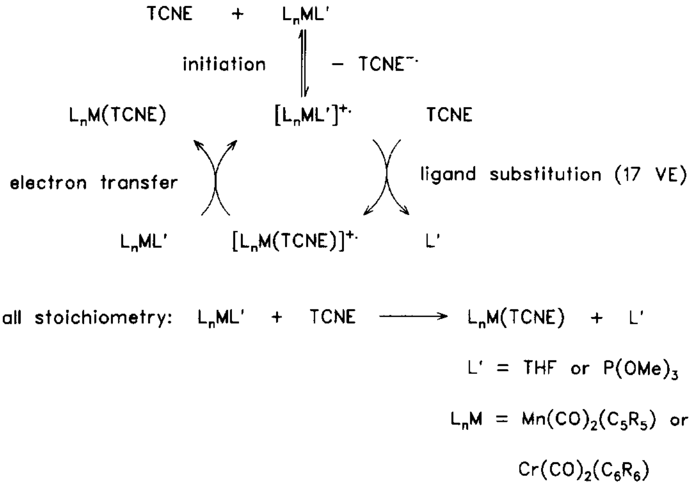
[27,47–51]. Depending inter alia on the ionization potential of the organometallic donor [11], the interaction with acceptors such as TCNX can lead to a complex with metal-to-TCNX charge transfer in the excited state or to complete electron transfer between the reaction partners in the ground state [11–13]. With main group organometallics, the pair of oppositely charged radical ions is often unstable because of disintegration of the cation radical [12,13,35(a)]; on the other hand, transition metal centres can tolerate odd-electron situations especially in a $3d^{2n-1}$ configuration and then form ion pairs or more tightly bound complexes with $TCNX^{-I}$ such as $(TCNE)VCp_2Hal$ [90]. 4d and 5d metal centres, with their preference for even-electron configurations, often tend to undergo two-electron transfer reactions, e.g. oxidative additions to d^8 systems such as Pt(II) complexes (eqn. (5)) or $Ir(CO)(PPh_3)_2Hal$ [8,113].

Another important factor in addition to the relative positions of acceptor and donor potentials is the space available for inner- or outer-sphere electron transfer [11]. While inner-sphere processes should be favoured here in view of the sterically "open" TCNX acceptors (Fig. 3), some very shielded organosilane donors were shown to undergo either outer-sphere electron transfer [36(a)] or no interaction at all [145], e.g. with the TCNE molecule [12,13] (Scheme 4).

A very attractive mechanism for the frequently observed "anomalously" rapid formation of TCNX complexes [27,43–46] is *self-induced electron transfer catalysis* [16,27,46], which, due to the very strong acceptor nature of the TCNX molecules, does not require external activation, e.g. by electrodes or chemical oxidants/reductants. A recent kinetic study on metal carbonyl complexes [46] showed that the η^1-coordinated complexes $(TCNE)Mn(CO)_2(C_5R_5)$ and $(TCNE)Cr(CO)_2(C_6Me_6)$ with a clearly reduced TCNE ligand are formed unusually quickly, whereas the η^2-coordinated compounds **1** with $M(CO)_5$ (M = Cr, W) and non-reduced TCNE are formed from solvate-precursor complexes in a normal, i.e. relatively slow, substitution reaction. A self-induced electron transfer catalysis according to Scheme 5 has been invoked to explain the former, more rapid substitution reactions [16,27,46]. The two requirements necessary for that cycle in terms of the electrochemical potentials are



Scheme 4.



Scheme 5.

the possibility of a homogeneous electron-transfer start reaction between the reaction partners and, secondly, a higher oxidation potential of the (TCNE^{-1})-containing product complex relative to the precursor compound.

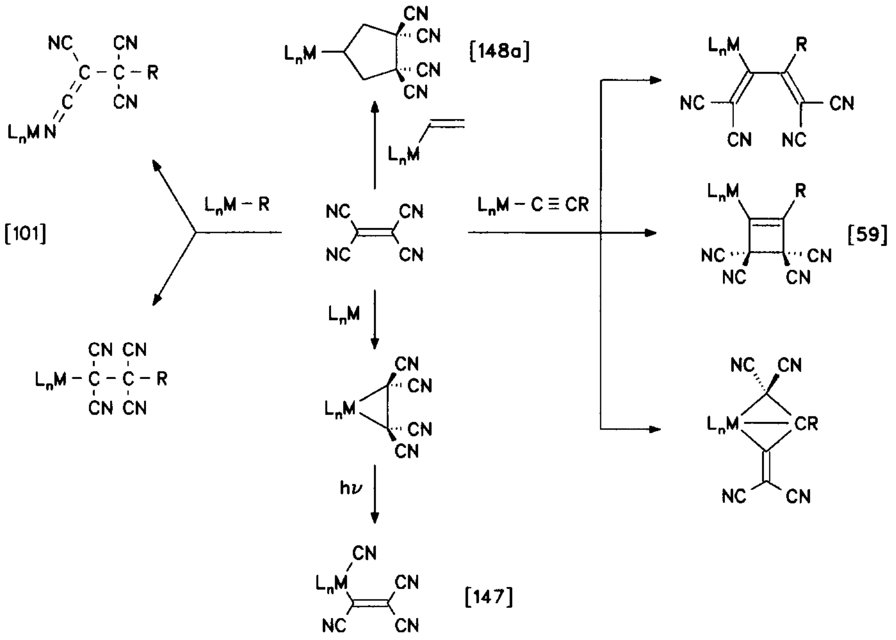
4.2 Bond-breaking reactions

In this article, we wish to refer only briefly to such reactions between metal compounds and TCNX which do not leave the TCNX molecules intact. Aspects of such less elementary reactivity were extensively discussed for TCNE in Fatiadi's reviews [7,14] and by Su and Wojicki [101]. Transition metal alkyls R–ML$_n$ and related compounds can add to TCNE in a variety of ways (1,2-, 1,4- or cycloaddition) as summarized in Scheme 6.

Many of these reactions involve intermediate coordination and/or electron transfer prior to the formation of the final product [7,11,51(b),59,101,146]. One very typical reaction which always has to be considered is the cleavage of a C–C bond to give cyanide and tricyanovinyl, which can serve as anionic ligand [146] or dimerize to HCBD^{2-} [29(a)]; other characteristic leaving groups are HCN and malonodinitrile [147(b)].

5. PHYSICAL PROPERTIES

Many complexes of the polynitrile ligands are distinguished by unusual physical properties which make them attractive for potential applications. Among these properties are anisotropic electrical conductivity (→"molecular metals"), ferromagnetism (→"molecular ferromagnets"), near-infrared absorption, non-linear optical be-



Scheme 6.

haviour and optical switching (→information recording and processing using diode lasers) and electron reservoir capacity (→catalysis).

5.1 Electrical conductance

Most work in this area has been directed to the formation of highly anisotropic conducting single crystals of solid state radical salts. TCNQ [148] and DCNQIs [10,19,20,71] are particularly suitable acceptor components in this field because of their tendency to undergo self-stacking and adopt non-integer oxidation states such as in the dimers $(TCNQ_2)^{-\cdot}$. Coordination polymers which exhibit ligand stacking, high solid-state symmetry [149] and an obvious electron transfer activity of non-isolated metal centres have turned out to be the most promising systems. While copper complexes of TCNQ have attracted a great deal of attention [21,58,76], the most striking results were obtained for $(2,5\text{-DMDCNQI})_2Cu$ [10]. This material contains partially reduced polynitrile molecules with pπ conduction band, partially oxidized (mixed-valent) metal centres Cu^{1+x} [71], and a special, easily perturbed [150] spatial arrangement in which, apparently, orbital mixing between both ligand stacks and linearly arranged metal centres can contribute to the remarkably high "metallic" but considerably anisotropic conductivity from 1000 S cm^{-1} at room temperature up to 500000 S cm^{-1} at 0.45 K [10,19,20,78].

Discrete metal coordination compounds with TCNX ligands are obviously less suitable for this kind of structurally supported one-dimensional electrical conductivity; detailed reviews on this subject are available [9,10,148].

5.2 Magnetism

The presence of spins on $TCNX^{-\cdot}$ ($S=1/2$) and on coordinated transition metal centres offers a wide variety of spin combinations and interactions, including cooperative magnetic behaviour. Of particular interest in recent years has been the possibility of designing molecular ferromagnetic materials. This field, pioneered by Miller et al. [18], involves charge transfer complexes of TCNX, e.g. with metallocenes such as $FeCp^*$ (bulk ferromagnet below 4.8 K [22]), linear chain coordination polymers such as **6** [26] and structurally yet-uncharacterized materials such as the room temperature ferrimagnet $V(TCNE)_x{\cdot}yCH_2Cl_2$, which was obtained by reacting $V(C_6H_6)_2$ with TCNE [24].

According to one model [22,151(a)], the configuration admixture of the lowest (metal-to-TCNX) charge transfer excited state with the ground state is responsible for the particular magnetic behaviour. Recently, an alternative concept was proposed [151(b)] involving the participation and interaction of the Cp* rings with neighbouring TCNX anion radicals.

While copper complexes of TCNQ have been another fruitful area of research [58], the variety of possible spin–spin interactions is best illustrated by complexes of $TCNE^{-I}$ with manganese compounds because low-valent Mn is distinguished by a tendency towards high-spin configurations. For instance, $TCNE^{-\cdot}$ ($S=1/2$) as ligand forms complexes with

(a) $[Mn^{III}(meso\text{-}TPP)]^+$ (h.s. d^4, $S=2$), exhibiting ferromagnetism below 18 K; this compound, 7, is a coordination polymer with $\mu;\eta^1:\eta^1$ coordinated $TCNE^{-\cdot}$ [26,93],

(b) $[Mn^{III}(PR_3)Hal_2]^+$ (h.s. d^4, $S=2$), which were described as containing η^1 coordinated $TCNE^{-\cdot}$ bound "end-on" to Mn centres of a halide-bridged chain [94],

(c) $[Mn^{III}Cp^*_2]^+$ (l.s. d^4; ion-paired charge transfer complex with ferromagnetic coupling below 8.8 K [23]), and

(d) $[Mn^{II}(CO)_2Cp^*]^+$ (metal-based paramagnetism (spin-crossover) *independent* of the presence of spin-paired $TCNE^{-I}$ ligand [95]).

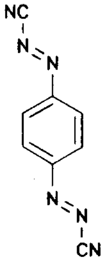
5.3 Optical properties

The similarity in energy between TCNX π^* orbitals and transition metal d levels and the often small orbital interaction can lead to narrow HOMO/LUMO gaps in corresponding complexes. Close-lying redox waves for partially reversible one- or two-electron oxidations or reductions [27,84] and long-wavelength charge transfer transitions result as a consequence of this situation. Polynuclear complexes, in particular, can show such transitions as very intense absorptions in the near-infrared region [143]; for instance, tetranuclear manganese [27] and ruthenium [66] complexes of μ_4-TCNX ligands show very strong ($\varepsilon > 50\,000\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$) absorption bands between 800 and 1600 nm.

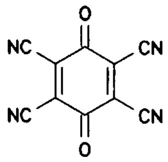
The polarizability of extended one-dimensional charge transfer salts involving, for example, TCNQ^{x-} also renders such systems suitable for purposes of non-linear optical activity and optical switching [28].

6. OUTLOOK

The simple polynitriles TCNE, TCNQ, TCNB and DCNQI are unique polydentate non-chelating ligands because they can exist in three different oxidation states at quite ordinary potentials and they can interact via several different coordination modes with metal centres, viz. via ion pairing, π or (polyhapto) σ binding. Complicated electronic structures arise not only from the structural alternatives and the different extent of electron transfer between these ligands and (transition) metal centres but also from the variable coupling of ligand and metal spins. There is no doubt that the unusual physical properties associated with some of these systems will further stimulate this very fruitful field of coordination chemistry, especially since slight modifications introduced can alter the physical properties enormously [150]. Substituted TCNQ systems, less studied polynitriles such as TCNB, TCNP or HCBD and newly designed and synthesized nitrile acceptors such as benzenebis(diazocyanides) (**14**) [152] or cyanil (**15**) [153] are further promising candidates to extend this fascinating field of coordination chemistry.



14



15

ACKNOWLEDGEMENTS

Support for this work has come from Deutsche Forschungsgemeinschaft (SFB 329) and Volkswagenstiftung. We would also like to thank many of our colleagues who have provided us with relevant information, in particular Joel S. Miller (University of Utah).

REFERENCES

1 E.C.M. Chen and W.E. Wentworth, J. Chem. Phys., 63 (1975) 3183.
2 M.E. Peover, Trans. Faraday Soc., 58 (1962) 2370.

3 H. Larsen, S.U. Pedersen, J.A. Pedersen and H. Lund, J. Electroanal. Chem., 331 (1992) 971.
4 F. Gerson, R. Heckendorn, D.O. Cowan, A.M. Kini and M. Maxfield, J. Am. Chem. Soc., 105 (1983) 7017.
5 C.K. Jorgensen, Oxidation Numbers and Oxidation States, Springer-Verlag, Berlin, 1969, p. 291.
6 W.H. Baddley, Inorg. Chim. Acta Rev., 2 (1968) 7.
7 A.J. Fatiadi, Synthesis, (1987) 959.
8 S.D. Ittel and J.A. Ibers, Adv. Organomet. Chem., 14 (1976) 33.
9 H. Endres, Extended Linear Chain Compounds, Vol. 3, Plenum Press, New York, 1983, p. 263.
10 S. Hünig and P. Erk, Adv. Mater., 3 (1991) 225.
11 J.K. Kochi, Organometallic Mechanisms and Catalysis, Academic Press, New York, 1978, Chaps. 15 and 16.
12 W. Kaim and B. Olbrich-Deussner, in W.C. Trogler (Ed.), Organometallic Radical Processes, Elsevier, Amsterdam, 1990, p. 173.
13 W. Kaim, in A. Müller, E. Diemann, W. Junge and H. Ratajczak (Eds.), Electron and Proton Transfer in Chemistry and Biology, Elsevier, Amsterdam, 1992, p. 45.
14 A.J. Fatiadi, Synthesis, (1986) 249; (1987) 749.
15 L.R. Melby, R.J. Harder, W.R. Hertler, W. Mahler, R.E. Benson and W. Mochel, J. Am. Chem. Soc., 84 (1962) 3374.
16 W. Kaim, B. Olbrich-Deussner, R. Gross, S. Ernst, S. Kohlmann and C. Bessenbacher, in M. Chanon (Ed.), Importance of Paramagnetic Organometallic Species in Activation, Selectivity and Catalysis, Kluwer, Dordrecht, 1989, p. 283.
17 M.L.H. Green, J. Qin and D. O'Hare, J. Organomet. Chem., 358 (1988) 375.
18 J.S. Miller, A.J. Epstein and W.M. Reiff, Acc. Chem. Res., 21 (1988) 114.
19 A. Aumüller, P. Erk, G. Klebe, S. Hünig, J.U. von Schütz and H.P. Werner, Angew. Chem., 98 (1986) 759; Angew. Chem. Int. Ed. Engl., 25 (1986) 740.
20 P. Erk, S. Hünig, J.U. von Schütz, H.P. Werner and H.C. Wolf, Angew. Chem., 100 (1988) 286; Angew. Chem. Int. Ed. Engl., 27 (1988) 267.
21 (a) M.B. Inoue, M. Inoue, Q. Fernando and K.W. Nebesny, J. Phys. Chem., 91 (1987) 527.
(b) M. Inoue and M.B. Inoue, J. Chem. Soc. Chem. Commun., (1984) 790.
22 (a) S. Chittipeddi, K.R. Cromack, J.S. Miller and A.J. Epstein, Phys. Rev. Lett., 58 (1987) 2695.
(b) J.S. Miller, J.C. Calabrese, H. Rommelmann, S.R. Chittipeddi, J.H. Zhang, W.M. Reiff and A.J. Epstein, J. Am. Chem. Soc., 109 (1987) 769.
23 W.E. Broderick, J.A. Thompson, E.P. Day and B.M. Hoffman, Science, 249 (1990) 401.
24 J.M. Manriquez, G.T. Yee, R.S. McLean, A.J. Epstein and J.S. Miller, Science, 252 (1991) 1415.
25 G.T. Yee, J.M. Manriquez, D.A. Dixon, R.S. McLean, D.M. Groski, R.B. Flippen, K.S. Narayan, A.J. Epstein and J.S. Miller, Adv. Mater., 3 (1991) 309.
26 J.S. Miller, J.C. Calabrese, R.S. McLean and A.J. Epstein, Adv. Mater., 4 (1992) 498.
27 (a) R. Gross and W. Kaim, Angew. Chem., 99 (1987) 257; Angew. Chem. Int. Ed. Engl., 26 (1987) 251.
(b) R. Gross-Lannert, W. Kaim and B. Olbrich-Deussner, Inorg. Chem., 29 (1990) 5046.
28 (a) R.S. Potember, T.O. Poehler and R.C. Benson, Appl. Phys. Lett., 41 (1982) 548.
(b) E.I. Kamitsos and W.M. Risen, Jr., Solid State Commun., 45 (1983) 165.
29 (a) W. Beck, R. Schlodder and K.H. Lechler, J. Organomet. Chem., 54 (1973) 303.

(b) G.T. Yee, J.C. Calabrese, G. Vazquez and J.S. Miller, Inorg. Chem., 32 (1993) 377.
(c) R. Schlodder and J.A. Ibers, Inorg. Chem., 13 (1974) 2870.
(d) E. Maverick, E. Goldfish, J. Bernstein, K.N. Trueblood, S. Swaminathan and R. Hoffmann, J. Am. Chem. Soc., 94 (1972) 3364.
30 M. Konno, T. Ishii and Y. Saito, Acta Crystallogr. Sect. B, 31 (1977) 163.
31 L. Shields, J. Chem. Soc. Faraday Trans. 2, 81 (1985) 1.
32 M. Pasquali, C. Floriani, A. Chiesi-Villa and C. Guastini, Inorg. Chem., 20 (1981) 349.
33 A. Flamini and N. Poli, Inorg. Chim. Acta, 150 (1988) 149.
34 T.V. Baukova, O.G. Ellert, L.G. Kuzmina, N.V. Dvortsova, D.A. Lemenovskii and A.Z. Rubezhov, Mendeleev Commun., (1991) 22.
35 H. Bock, C. Näther and K. Ruppert, Z. Anorg. Allg. Chem., 614 (1992) 109.
(b) H. Bock and K. Ruppert, Inorg. Chem., 31 (1992) 5094.
36 (a) J. Baumgarten, C. Bessenbacher, W. Kaim and T. Stahl, J. Am. Chem. Soc., 111 (1989) 2126, 5017.
(b) H. Masai, K. Sonogashira and N. Hagihara, J. Organomet. Chem., 34 (1972) 397.
37 (a) V.F. Traven and R. West, J. Am. Chem. Soc., 95 (1973) 6824.
(b) H. Sakurai, M. Kira and T. Uchida, J. Am. Chem. Soc., 95 (1973) 6825.
(c) H. Watanabe, T. Muraoka, M. Kageyama, K. Yoshizumi and Y. Nagai, Organometallics, 3 (1984) 141.
38 (a) J.W. Fitch and J.J. Lagowski, Inorg. Chem., 4 (1965) 864.
(b) R.L. Brandon, J.H. Osiecki and A. Ottenberg, J. Org. Chem., 31 (1966) 1214.
(c) E. Adman, M. Rosenblum, S. Sullivan and T.N. Margulis, J. Am. Chem. Soc., 89 (1967) 4540.
(d) A.K. Holliday, P.H. Makin, R.J. Puddephatt and J.D. Wilkins, J. Organomet. Chem., 57 (1973) C45.
39 D.A. Dixon and J.S. Miller, J. Am. Chem. Soc., 109 (1987) 3656.
40 S.Z. Goldberg, B. Spivack, G. Stanley, R. Eisenberg, D.M. Braitsch, J.S. Miller and M.A. Abkowitz, J. Am. Chem. Soc., 99 (1977) 110.
41 M.D. Ward and D.C. Johnson, Inorg. Chem., 26 (1987) 4213.
42 P. Baird, J.A. Bandy, M.L.H. Green, A. Hamnett, E. Marseglia, D.S. Obertelli, K. Prout and J. Qin, J. Chem. Soc. Dalton Trans., (1991) 2377.
43 K. Iuchi, S. Asada, T. Kïnugasa, K. Kanamori and A. Sugimori, Bull. Chem. Soc. Jpn., 49 (1976) 577.
44 J.R. Morrow, T.L. Tonker and J.L. Templeton, J. Am. Chem. Soc., 107 (1985) 6956.
45 K.L. Amos and N.G. Connelly, J. Organomet. Chem., 194 (1980) C57.
46 B. Schwederski, W. Kaim, B. Olbrich-Deussner and T. Roth, J. Organomet. Chem., 440 (1992) 145.
47 M. Haga, K. Kawakami and T. Tanaka, Inorg. Chem., 15 (1976) 1946.
48 N.G. Connelly, R.G. Kelly and M.W. Whiteley, J. Chem. Soc. Dalton Trans., (1981) 34.
49 A.L. Balch, J. Am. Chem. Soc., 98 (1976) 285.
50 S.D. Ittel, C.A. Tolman, P.J. Krusic, A.D. English and J.P. Jesson, Inorg. Chem., 17 (1978) 3432.
51 (a) J.-M. Giraudon, J.-E. Guerchais, J. Sala-Pala and L. Toupet, J. Chem. Soc. Chem. Commun., (1988) 921.
(b) M.I. Bruce, T.W. Hambley, M.R. Snow and A.G. Swincer, Organometallics, 4 (1985) 501.
52 (a) M.D. Ward, P.J. Fagan, J.C. Calabrese and D.C. Johnson, J. Am. Chem. Soc., 111 (1989) 1719.
(b) P.J. Fagan and M.D. Ward, Sci. Am., 267 (July 1992) 28.

(c) J. Tanaka, M. Tanaka, T. Kawai, T. Takabe and O. Maki, Bull. Chem. Soc. Jpn., 49 (1976) 2358.
(d) A. Bencini and C. Zanchini, Inorg. Chem., 30 (1991) 4245.
53 Y. Yamamoto and H. Yamazaki, Inorg. Chim. Acta, 85 (1983) 83.
54 A.E.D. McQueen, A.J. Blake, A. Stephenson, M. Schröder and L.J. Yellowlees, J. Chem. Soc. Chem. Commun., (1988) 1533.
55 H. Braunwarth, G. Huttner and L. Zsolnai, J. Organomet. Chem., 372 (1989) C23.
56 D.G. Humphrey, G.D. Fallon and K.S. Murray, J. Chem. Soc. Chem. Commun., (1988) 1356.
57 P. Lacroix, O. Kahn, A. Gleizes, L. Valade and P. Cassoux, Nouv. J. Chim., 8 (1984) 643.
58 (a) S.K. Hoffmann, P.J. Corvan, P. Singh, C.N. Sethulekshmi, R.M. Metzger and W.E. Hatfield, J. Am. Chem. Soc., 105 (1983) 4608.
(b) M. Schwartz and W.E. Hatfield, Inorg. Chem., 26 (1987) 2823.
59 M.I. Bruce, T.W. Hambley, M.R. Snow and A.G. Swincer, Organometallics, 4 (1985) 494.
60 J.A. Connor and P.I. Riley, J. Organomet. Chem., 174 (1979) 173.
61 T. Roth, Ph.D. Thesis, University of Stuttgart, 1992.
62 B. Olbrich-Deussner, R. Gross and W. Kaim, J. Organomet. Chem., 366 (1989) 155.
63 T. Roth and W. Kaim, Inorg. Chem., 31 (1992) 1930.
64 D.M. Hoffman and S. Lee, Inorg. Chem., 31 (1992) 2675.
65 S.I. Amer, T.P. Dasgupta and P.M. Henry, Inorg. Chem., 22 (1983) 1970.
66 M. Moscherosch and W. Kaim, Inorg. Chim. Acta, 206 (1993) 229; unpublished results, 1993.
67 A. Schulz, J. Poppe and W. Kaim, unpublished results, 1992.
68 (a) K.S. Chen and J.K.S. Wan, J. Am. Chem. Soc., 100 (1978) 6051.
(b) P.G. Harrison and O.A. Idowu, Inorg. Chim. Acta, 81 (1984) 213.
(c) A.B. Cornwell, P.G. Harrison and J.A. Richards, J. Organomet. Chem., 140 (1977) 273.
69 A. Rockenbauer, G. Speier and L. Szabo, Inorg. Chim. Acta, 201 (1992) 9.
70 M. Ladwig and W. Kaim, J. Organomet. Chem., 439 (1992) 79.
71 (a) D. Schmeisser, K. Graf, W. Göpel, J.U. von Schütz, P. Erk and S. Hünig, Chem. Phys. Lett., 148 (1988) 423.
(b) M. Helmle, J. Reiner, U. Rempel, M. Mehring, J.U. von Schütz, P. Erk, S. Hünig and H. Meixner, Synth. Met., 42 (1991) 1763.
(c) A. Kobayashi, R. Kato, H. Kobayashi, T. Mori and H. Inokuchi, Solid State Commun., 64 (1987) 45.
72 B. Olbrich-Deussner, Ph.D. Thesis, University of Stuttgart, 1989.
73 J.S. Chappell, A.N. Bloch, W.A. Bryden, M. Maxfield, T.O. Poehler and D.O. Cowan, J. Am. Chem. Soc., 103 (1981) 2442.
74 T. Yamamoto, A. Yamamoto and S. Ikeda, J. Am. Chem. Soc., 93 (1971) 3350.
75 W. Kaschube, K.R. Pörschke and G. Wilke, J. Organomet. Chem., 355 (1988) 525.
76 M. Inoue and M.B. Inoue, J. Chem. Soc. Faraday Trans. 2, 81 (1985) 539.
77 C.G. Pierpont and R.M. Buchanan, Coord. Chem. Rev., 38 (1981) 45.
78 P. Erk, H. Meixner, T. Metzenthin, S. Hünig, U. Langohr, J.U. von Schütz, H.-P. Werner, H.C. Wolf, R. Burkert, H.W. Helberg and G. Schaumburg, Adv. Mater., 3 (1991) 311.
79 R.C. Haddon, Aust. J. Chem., 28 (1975) 2333.
80 H. Krentzien and H. Taube, J. Am. Chem. Soc., 98 (1976) 6379; Inorg. Chem., 21 (1982) 4001.
81 M.P. Eastman, D.A. Ramirez, C.D. Jaeger and M.T. Watts, J. Phys. Chem., 80 (1976) 182.
82 M. Herberhold, Angew. Chem., 84 (1972) 773.
83 M. Herberhold, Angew. Chem., 80 (1968) 314; Angew. Chem. Int. Ed. Engl., 7 (1968) 305.

84 B. Olbrich-Deussner, W. Kaim and R. Gross-Lannert, Inorg. Chem., 28 (1989) 3113.
85 W. Kaim, B. Olbrich-Deussner and T. Roth, Organometallics, 10 (1991) 410.
86 D.J. Stufkens, T.L. Snoeck, W. Kaim, T. Roth and B. Olbrich-Deussner, J. Organomet. Chem., 409 (1991) 189.
87 B. Demerseman, M. Pankowski, G. Bouquet and M. Bigorgne, J. Organomet. Chem., 117 (1976) C10.
88 S.E. Bell, J.S. Field, R.I. Haines, M. Moscherosch, W. Matheis and W. Kaim, Inorg. Chem., 31 (1992) 3269.
89 M.S. Fraser, G.F. Everitt and W.H. Baddley, J. Organomet. Chem., 35 (1972) 403.
90 M.F. Rettig and R.M. Wing, Inorg. Chem., 8 (1969) 2685.
91 A.L. Crumbliss and F. Basolo, Inorg. Chem., 10 (1971) 1676.
92 W. Kaim, Coord. Chem. Rev., 76 (1987) 187.
93 D.A. Summerville, T.W. Cape, E.D. Johnson and F. Basolo, Inorg. Chem., 17 (1978) 3297.
94 G.A. Gott and C.A. McAuliffe, J. Chem. Soc. Dalton Trans., (1987) 1785.
95 W. Kaim, T. Roth, B. Olbrich-Deussner, R. Gross-Lannert, J. Jordanov and E.K.H. Roth, J. Am. Chem. Soc., 114 (1992) 5693.
96 J.P. Collman, L.S. Hegedus, J.R. Norton and R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1937.
97 (a) A. Evans, C.T. Mortimer and R.J. Puddephatt, J. Organomet. Chem., 72 (1974) 295.
(b) C.T. Mortimer, M.P. Wilkinson and R.J. Puddephatt, J. Organomet. Chem., 165 (1979) 269.
98 H.C. Clark and R.J. Puddephatt, Inorg. Chem., 10 (1971) 416.
99 M. Bottrill, M. Green, A.G. Orpen, D.R. Saunders and I.D. Williams, J. Chem. Soc. Dalton Trans., (1989) 511.
100 R.D. Adams and D.F. Chodosh, J. Am. Chem. Soc., 99 (1977) 6544.
101 S.R. Su and A. Wojcicki, Inorg. Chem., 14 (1975) 89.
102 S.M. Grant and A.R. Manning, J. Chem. Soc. Dalton Trans., (1979) 1789.
103 M.O. Albers, N.J. Coville and E. Singleton, J. Chem. Soc. Dalton Trans., (1982) 1069.
104 H.C. Ashton and A.R. Manning, Inorg. Chem., 22 (1983) 1440.
105 E. Lindner, R.-M. Jansen, H.A. Mayer, W. Hiller and R. Fawzi, Organometallics, 8 (1989) 2355.
106 (a) T. Kaneshima, K. Kawakami and T. Tanaka, Inorg. Chem., 13 (1974) 2198.
(b) K. Kawakami, K. Ishii and T. Tanaka, Bull. Chem. Soc. Jpn., 48 (1975) 1051.
107 H. Werner and B. Juthani, J. Organomet. Chem., 209 (1981) 211.
108 F. Faraone, S.L. Schiavo, G. Bruno, P. Piraino and G. Bombieri, J. Chem. Soc. Dalton Trans., (1983) 1813.
109 M.I. Bruce, T.W. Hambley, M.R. Snow and A.G. Swincer, J. Organomet. Chem., 235 (1982) 105.
110 T. Kaneshima, Y. Yumoto, K. Kawakami and T. Tanaka, Inorg. Chim. Acta, 18 (1976) 29.
111 J.B.R. Dunn, R. Jacobs and C.J. Fritchie, J. Chem. Soc. Dalton Trans., (1972) 2007.
112 J.A. McGinnety and J.A. Ibers, J. Chem. Soc. Chem. Commun., (1968) 235.
113 J.S. Ricci and J.A. Ibers, J. Am. Chem. Soc., 93 (1971) 2391.
114 B. Corain, L. DeNardo and G. Favero, J. Organomet. Chem., 125 (1977) 105.
115 (a) P. Fitton and J.E. McKeon, J. Chem. Soc. Chem. Commun., (1968) 4.
(b) M. Hodgson, D. Parker, R.J. Taylor and G. Ferguson, J. Chem. Soc. Chem. Commun., (1987) 1309.
116 C. Panattoni, G. Bombieri, U. Belluco and W.H. Baddley, J. Am. Chem. Soc., 90 (1968) 798.
117 R. Bertani, G. Carturan, A. Scrivanti and A. Wojcicki, Organometallics, 4 (1985) 2139.
118 A. Johnson and R.J. Puddephatt, J. Chem. Soc. Dalton Trans., (1977) 1384.

119 G.L. Geoffroy and M.S. Wrighton, Organometallic Photochemistry, Academic Press, New York, 1979.

120 A.R. Siedle, G.A. Candela and T.F. Finnegan, Inorg. Chim. Acta, 35 (1979) 125.

121 S.G. Clarkson, B.C. Lane and F. Basolo, Inorg. Chem., 11 (1972) 662.

122 (a) P.H. Rieger, I. Bernal and G.K. Fraenkel, J. Am. Chem. Soc., 83 (1961) 3918.
(b) P.H. Rieger and G.K. Fraenkel, J. Chem. Phys., 37 (1962) 2795.

123 T. van Houwelingen, D.J. Stufkens and A. Oskam, Coord. Chem. Rev., 111 (1991) 325.

124 S.A. Lerke, B.A. Parkinson, D.H. Evans and P.J. Fagan, J. Am. Chem. Soc., 114 (1992) 7807.

125 P.J. Krusic, H. Stoklasa, L.E. Manzer and P. Meakin, J. Am. Chem. Soc., 97 (1975) 667.

126 M.J. Macazaga, M.S. Delgado and J.R. Masaguer, J. Organomet. Chem., 310 (1986) 249.

127 N.G. Connelly, in G. Wilkinson (Ed.), Comprehensive Organometallic Chemistry, Vol. 3, Pergamon Press, Oxford, 1982, p. 647.

128 F.G. Moers and J.P. Langhout, J. Inorg. Nucl. Chem., 39 (1977) 591.

129 W. Matheis, Ph.D. Thesis, University of Stuttgart, 1993.

130 B.L. Booth, C.A. McAuliffe and G.L. Stanley, J. Chem. Soc. Dalton Trans., (1982) 535.

131 S. Fukuzumi, K. Mochida and J.K. Kochi, J. Am. Chem. Soc., 101 (1979) 5961.

132 B.E.R. Schilling, R. Hoffmann and D.L. Lichtenberger, J. Am. Chem. Soc., 101 (1979) 585.

133 M.I. Bruce, T.W. Hambley, M.J. Liddell, A.G. Swincer and E.R.T. Tiekink, Organometallics, 9 (1990) 2886.

134 (a) R.E. Clarke and P.C. Ford, Inorg. Chem., 9 (1970) 495.
(b) P.C. Ford, R.D. Foust, Jr. and R.E. Clarke, Inorg. Chem., 9 (1970) 1933.

135 J.P. Cornelissen, J.H. van Diemen, L.R. Groeneveld, J.G. Haasnoot, A.L. Spek and J. Reedijk, Inorg. Chem., 31 (1992) 198.

136 T. Ito, S. Kitazume, A. Yamamoto and S. Ikeda, J. Am. Chem. Soc., 92 (1970) 3011.

137 L. Ballester, M.C. Barral, A. Gutierrez, R. Jimenez-Aparicio, J.M. Martinez-Muyo, M.F. Perpinan, M.A. Monge and C. Ruiz-Valero, J. Chem. Soc. Chem. Commun., (1991) 1396.

138 A.B. Cornwell, C.A. Cornwell and P.G. Harrison, J. Chem. Soc. Dalton Trans., (1976) 1612.

139 W. Sacher, U. Nagel and W. Beck, Chem. Ber., 120 (1987) 895.

140 P. Alonso, E. Cerrada, J. Garin, M.C. Gimeno, P.G. Jones, A. Laguna and M. Laguna, International Conference on Science and Technology of Synthetic Materials, Göteborg, Sweden, 1992, Abstr. No. ET/G 25,S.

141 A.G. Bunn, P.J. Carroll and B.B. Wayland, Inorg. Chem., 31 (1992) 1297.

142 (a) M.M. Olmstead, G. Speier and L. Szabo, submitted for publication.
(b) Y.-S. Huang, S. Sabo-Etienne, X.-D. He, B. Chaudret, K. Boubekeur and P. Batail, Organometallics, 11 (1992) 3031.

143 S.L. Bartley and K.R. Dunbar, Angew. Chem., 103 (1991) 447; Angew. Chem. Int. Ed. Engl., 30 (1991) 448.

144 M.C. Grossel, F.A. Evans, J.A. Hriljac, J.R. Morton, Y. LePage, K.F. Preston, L.H. Sutcliffe and A.J. Williams, J. Chem. Soc. Chem. Commun., (1990) 439. See also M.C. Grossel and S.C. Weston, J. Chem. Soc. Chem. Commun., (1992) 1510.

145 H. Bock, W. Kaim and H.-E. Rohwer, Chem. Ber., 111 (1978) 3573.

146 O. Traverso, V. Carassiti, M. Graziani and U. Belluco, J. Organomet. Chem., 57 (1973) C22.

147 (a) P.B. Bell and A. Wojcicki, Inorg. Chem., 20 (1981) 1585.
(b) M. Etienne and L. Toupet, J. Chem. Soc. Chem. Commun., (1989) 1110.

148 J.B. Torrance, Acc. Chem. Res., 12 (1979) 79.

149 O. Ermer, Adv. Mater., 3 (1991) 608.

150 S. Hünig, K. Sinzger, M. Jopp, D. Bauer, W. Bietsch, J.U. von Schütz and H.C. Wolf, Angew. Chem., 104 (1992) 896; Angew. Chem. Int. Ed. Engl., 31 (1992) 859.

151 (a) H.M. McConnell, Proc. Robert A. Welch Found. Conf. Chem. Res., 11 (1967) 144. (b) C. Kollmar, M. Couty and O. Kahn, J. Am. Chem. Soc., 113 (1991) 7994. See also J. Blümel, N. Hebendanz, P. Hudeczek, F.H. Köhler and W. Strauss, J. Am. Chem. Soc., 114 (1992) 4223 and D.M. Eichhorn, D.C. Skee, W.E. Broderick and B.M. Hoffman, Inorg. Chem., 32 (1993) 491.

152 H. Almen, T. Bauer, S. Hünig, V. Kupcik, U. Langohr, T. Metzenthin, K. Meyer, H. Rieder, J.U. von Schütz, E. Tillmanns and H.C. Wolf, Angew. Chem., 103 (1991) 608; Angew. Chem. Int. Ed. Engl., 30 (1991) 561.

153 C. Vazquez, J.C. Calabrese, D.A. Dixon and J.S. Miller, J. Org. Chem., 58 (1993) 65.