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PERSPECTIVE

Cyanide-bridged oligonuclear complexes: features and attractions†

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The synthetic and structural chemistry as well as some physical and chemical properties of cyanide-bridged complexes containing two or more metal building blocks are discussed. Emphasis is laid on molecular shape and design and their consequences, including the effects of cyanide–isocyanide isomerism. Redox phenomena and molecular magnetism have been dealt with in relation to electronic communication across the cyanide bridges and metal–metal charge transfer. Long-range interactions between remote metal centers are discussed, and the few cases where they lead to remote chemical reactions are listed.

Prussian Blue, $[Fe_4\{Fe(CN)_6\}_3]\cdot xH_2O$, which actually is the oldest known co-ordination compound,[1] has attracted the skills of many scientists seeking an understanding of its formation and composition,[2] structure,[3] colour[4] and physical properties like magnetism[5] and electrical conductivity.[6] Although it was soon obvious that the linking of two different metal ions by the cyanide ligand is the basis of all these phenomena, this did not initiate a variation of the theme. The systematic synthetic and physical exploration of Prussian Blue-like compounds had to await the popularity of the chemistry of materials. Only in recent years has a number of attractive two- and three-dimensional co-ordination polymers comprised of M−CN−M′ units been prepared and subjected to the appropriate measurements.[7]

While bulk magnetism and conductivity require extended interactions their basic fundamental property, the electronic communication between two metals across the cyanide bridge, is local and can be studied in simple dinuclear complexes. But classical co-ordination chemistry was not interested in this phenomenon, and hence the literature of more than 25 years ago contains only rare examples of cyanide-bridged systems[8] amongst the multitude of ligand-bridged dinuclear complexes.[9] It took the emerging discussion of mixed valence[10–12] and inner-sphere electron transfer[13,14] to move the M−CN−M′ systems into the limelight. They were among the first to be studied in this respect,[15,16] and since then the electronic interactions between two metals across a cyanide bridge have proven to be a fertile area of research.

In the last 15 years many di- and tri-nuclear complexes with bridging cyanide ligands have been investigated for the electronic communication and the electron transfer between their metal centers by means of electronic spectroscopy, electrochemistry, IR spectroscopy, fast kinetic methods and molecular orbital (MO) theory. Among others, the research groups of Haim,[17] Vogler,[18] Scandola,[19] Bocarsly,[20] Meyer,[21] Endicott,[22] Riera,[23] Connelly,[24] and Denning,[25] (each being represented by the most recent publication) have made major contributions, the results of which have also been extracted into review articles.[26–30] Today the literature on cyanide-bridged oligonuclear complexes consists of some 250 papers, and in addition to the ones mentioned above[26–30] an extensive collection of reviews[10–12,31–37] contains discussions of their formation and properties.

At first glance there shouldn't be much reason to write another review. Yet we have written one, and we think it is timely to do so. In our opinion this field of research is reaching a major step in its evolution, the step from an understanding of its basic features to their exploitation. The recent outbreak in the design of magnetic materials[7] may serve as an example. We view the construction and application of molecular units containing arrays of cyanide-linked metal centers as a main line for future development, and we want to focus attention on it. We are presenting our personal opinions and preferences by selecting the topics of discussion and the corresponding references, and we refrain from discussing subjects which, in our opinion, have been discussed thoroughly enough in the recent literature.

Specifically, this review will not deal with features related to two- and three-dimensional polymers, *e.g.* structures and physical properties of metal- and cyanide-containing materials, nor the application of cyanometal compounds in energy conversion, *e.g.* light harvesting. Very little attention will be given to spectroscopy-related topics, *e.g.* ν(CN) band positions, metal-to-metal charge transfer absorptions and UV/VIS/NIR spectroscopy, and photoinduced electron transfer. Similarly the more physically oriented topics, *e.g.* electron transfer kinetics, ultrafast spectroscopy, and MO theory, will be neglected.

The main subjects of this review are molecular complexes containing several M−CN units linked together, the ways of making M−CN−M′ links and their consequences, and the attractions resulting from mastering the design of cyanometal arrays. The focus is more on basic knowledge than on applications, and the beauty of a formula drawing will suffice to show it. The outcome of all the chemistry presented here will have to be limited to physical and chemical properties, and our wish to indicate how these may arise. We want to direct attention to the challenges which have not been satisfactorily met and thereby stimulate the corresponding scientific activity.

Molecular Shape and Design

Oligonuclear complexes with cyanide bridges can have many different shapes because the connectivity of a single metal unit M can be as variable as the number of cyanide ligands in the simple cyanometal complexes $L_mM(CN)_n$. The fact that the cyanide ion has similar good donor qualities at both its C and N atoms[31] therefore makes the construction of oligonuclear metallocyanides a game that is comparable to synthetic organic or main-group element chemistry. Its only limitation is the lability of many metal complexes. Bearing this in mind an enormous range of compositions and shapes can be envisaged of which only a few have been realized. The use of organometallic building blocks with their higher inertness should further widen the scope. With this background it is actually amazing how little the synthetic opportunities in this field have been exploited.

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† *Non-SI unit employed:* $\mu_B \approx 9.274 \times 10^{-24}$ J T^{-1}.

Principles

The basic construction principle is trivial and involves the use of a cyanometal complex, M−CN, as a ligand for a second complex unit M′. Accordingly, by far the greatest class of oligonuclear cyanometal complexes is the dinuclear ones of the type M−CN−M′. Except for the discussion of some special features we will not deal with them here. The construction principle has to be applied in the same way for trinuclear and higher nuclearity complexes. This involves the use of di- or polyfunctional reagents which have to be handled correctly in order to avoid the formation of intractable polymers.

It is still easy to envisage the combination of one polyfunctional reagent with the corresponding number of monofunctional partners leading to complexes $(M-CN)_nM'$ (type **1**) and $M(CN-M')_n$ (type **2**) with the polyfunctional building block in the center. Most of the trinuclear and all star-like and cluster-derived metallocyanides (see below for some examples) have been made in this way.

Things get more complicated when trying to construct linear tetranuclear or unsymmetrical trinuclear complexes. This either requires the stepwise attachment of monofunctional units to a difunctional unit, *e.g. via* intermediates M′−NC−M−CN **3**, or the construction of intermediates like M−CN−M′−CN **4** with C- and N-co-ordinated cyanide ligands at the same metal. Both alternatives have been realized in only a few cases so far, and their controlled handling is the major challenge in this area. Attachment of intermediates like **3** or **4** to a central difunctional unit would lead to linear pentanuclear complexes, but this has not yet been done. Similarly, linear complexes of higher nuclearity are still unknown. Formula **4**, however, visualizes how a suitable combination of identical L_nM-CN units having one open co-ordination site can lead to one-dimensional polymers.

The combination of two difunctional building blocks, *e.g.* $M(CN)_2$ and L_2M' (L = replaceable ligand), must lead to rings or polymers. As the examples below show, this has rarely been done successfully. Similarly, the construction of cages requires trifunctional building blocks and a lot of luck. Cyanometal cages are known but more often three-dimensional polymers have been obtained.[7,30] One cannot say at the moment how to design the right building blocks for cyanometal cages, but Mother Nature helps sometimes with self-assembly.

Cyanide–isocyanide isomerism

The question of cyanide–isocyanide isomerism (M−CN−M′ *vs.* M−NC−M′) is as old as the discussion of the structure of Prussian Blue. While it is now known that in Prussian Blue cyanide is always C-bonded to Fe^{II} and N-bonded to Fe^{III},[3] examples for this kind of isomerism have been found in Prussian Blue analogues and oligonuclear complexes. The oldest observations date back some 30 years when Shriver and co-workers found the thermal isomerisations of Fe–Cr, Fe–Mn and Co–Cr Prussian Blue analogues by a combination of spectroscopic, X-ray and magnetic measurements,[38–40] to which was later added the isomerisation of a related Cd–Fe compound.[41]

Among the molecular complexes the first pair of isomers, $[(H_3N)_5Co(\mu\text{-}CN)Co(CN)_5]$ **5a** and $[(H_3N)_5Co(\mu\text{-}NC)Co(CN)_5]$ **5b**, was prepared by Haim and co-workers[42,43] and subsequently complemented by the analogous pair containing $(H_2O)_5Cr$ in place of $(H_3N)_5Co$.[44] We contributed a series of stable pairs containing organometallic building blocks[45] including the structurally characterized pair $[(OC)_5Cr(\mu\text{-}CN)Fe(dppe)Cp]$ [dppe = 1,2-bis(diphenylphosphino)ethane, Cp = η^5-C_5H_5] **6a** and $[(OC)_5Cr(\mu\text{-}NC)Fe(dppe)Cp]$ **6b**.[46] Other pairs of dinuclear complexes containing the metal combinations Au–Rh and Au–Ir,[47] Mn–Mn,[48] W–Cu,[49] and Re–Ru[50] have been described. In some cases spontaneous isomerization leaving only one of the isomers is observed.[47,49]

Cyanide–isocyanide isomerism was also found in trinuclear complexes. The first case involved the solvent-dependent equilibration between $[(OC)_5Cr(\mu\text{-}CN)Hg(\mu\text{-}NC)Cr(CO)_5]$ **7a** and $[(OC)_5Cr(\mu\text{-}NC)Hg(\mu\text{-}CN)Cr(CO)_5]$ **7b**.[51] More recently two cases of complexes containing central $Ru(bipy)_2$ (bipy = 2,2′-bipyridine) units were described for which both isomers could be isolated. In both the $RuRe_2$ and the $RuCr_2$ complexes $(bipy)_2Ru[RRe(CO)_3bipy]_2{}^{2+}$ **8** (R = μ-NC **8a** or R = μ-CN **8b**)[52] and $(bipy)_2Ru[RCr(cyclam)CN]_2{}^{4+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) **9** (R = μ-NC **9a** or R = μ-CN **9b**)[19] the isomers **b** having both cyanide C atoms attached to ruthenium are more stable and are accessible by thermal isomerization. We have contributed to the first case of such an isomerism where a cyanide and an isocyanide linkage between two identical pairs of metal–ligand units are the result of the isomerization. Both the phthalocyanine iron complexes $Cp(Ph_3P)_2Ru(\mu\text{-}CN)Fe(pc)(\mu\text{-}NC)Ru(PPh_3)_2Cp$ (pc = phthalocyanine) **10a** and $Cp(Ph_3P)_2Ru(\mu\text{-}CN)Fe(pc)(\mu\text{-}CN)Ru(PPh_3)_2Cp$ **10b** have been characterized by structure determination.[53]

Chains

If one wants to realize the promise of cyanide-linked metal units, namely extended interactions and long-range electron transfer, one has to build chain-like complexes containing arrays of several M−CN entities. This has been done for quite a number of trinuclear compounds, most of which are of the symmetrical types **1** and **2** with $n = 2$. We shall list the references for all of them but limit the discussion to some special cases.

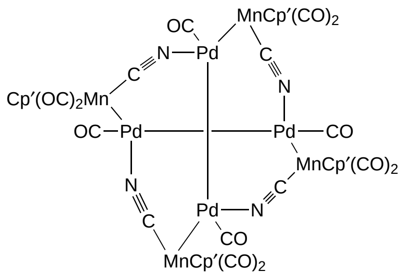
One may say that systematic research in this field was initialized by Siebert's discovery of the monofunctional cyanide complex $[Co(NH_3)_5CN]^{2+}$ and his observation that it acts as a ligand L in the 'supercomplexes' AgL_2 and HgL_2.[54] These represent the simplest type of trinuclear metallocyanides. A limited number of such complexes with the central metal ions Co, Ni, Cu, Ag, Au, Zn, Cd and Hg has since been prepared.[24,47,51,55]

By far the largest number of trinuclear complexes were investigated with light-induced electron transfer in mind, they therefore contain Ru(bipy) or similar units capable of photoinduced charge separation.[18–22,50,52,56–80] A somewhat heterogeneous collection of other complexes was prepared either for testing synthetic concepts, spectroscopic trends, redox properties or in relation to biochemical or materials properties.[24,25,53,81–88] Most of them contain an octahedral metal in the central position which is either *cis* or *trans* co-ordinated by the two other cyanometal units.

The number of unsymmetrical trinuclear complexes is still so low that those which were isolated and fully characterized can all be shown: $[(py)(NH_3)_4Ru-NC-Ru(bipy)_2-CN-Ru(NH_3)_5]^{6+}$ **11** (py = pyridine),[62] $[(phen)(CO)_3Re-CN-Ru(bipy)_2-CN-Ru(bipy)_2CN]^{2+}$ **12** (phen = 1,10-phenanthroline),[72] $[(H_3N)_5Co-NC-Co(CN)_4-CN-Ru(CN)_5]^{3-}$ **13**,[57] $[(H_3N)_5Ru-NC-Ru(CN)_4-CN-Co(NH_3)_5]^{2+}$ **14**[58] and $[Cp(dppe)Fe-NC-Pt(CN)_2-CN-Ru(PPh_3)_2Cp]$ **15**.[88] The lability of some of the classical complexes made their handling difficult.[68] We found again that this problem does not exist for the organometallic species and that complexes like **15** can easily be prepared in a stepwise manner.

We are not aware of a single case of two isomeric trinuclear complexes differing only in the *cis* or *trans* arrangement of the cyanide bridges at the central metal atom. It would be interesting to have such pairs to test the electronic communication between the two outer metals 'linear' or 'round the corner'. Therefore it is worth mentioning that there seem to be two cases where a slight variation of the ligand set at the central metal allows this modification, thereby making the *trans* isomers *trans*-$[(py)_4Ru\{NC-Ru(py)_4Cl\}_2]^{2+}$ **16a**[21] and $[(py)_2Pt\{NC-Fe(dppe)Cp\}_2]$ **17a**[88] comparable to their *cis* analogues *cis*-$[(bipy)_2Ru\{NC-Ru(bipy)_2CN\}_2]^{2+}$ **16b**[64] and $[(bipy)Pt\{NC-Fe(dppe)Cp\}_2]$ **17b**.[88]

Beyond the trinuclear complexes the synthetic terrain becomes difficult, and fully confirmed examples of species with chain-like arrays of more than three M−CN units are still



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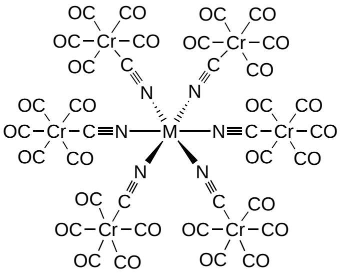

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missing. The only ones mentioned ($[(phen)(OC)_3ReCN\{Ru(bipy)_2CN\}_nRu(bipy)_2CN]^{(n+1)+}$ ($n = 2$ or 3)[72] **18**) could not be isolated as pure solids. There are, however, a few tetranuclear complexes containing a central dimetal unit which is not held together by a cyanide bridge. Connelly and co-workers[89] reported a series of Rh_2Mn_2 complexes $[L_mMn(CN)\{Rh_2(tz)_2\}(NC)MnL_m]^+$ **19** based on the central bis(triazenido)dirhodium unit $Rh_2(tz)_2$, and Braunstein *et al.*[90] found a similar Pd_2Mn_2 complex based on a central $Pd_2(dpm)_2$ [dpm = bis(diphenylphosphino)methane] unit. We found that two cyanometal units can be attached to a dimeric (salen) iron center to form complexes like $[Cp(dppe)Fe-CN\{Fe_2(salen)_2\}NC-Fe(dppe)Cp]^{2+}$ **20**[53] [H_2-salen = *N*,*N′*-bis(salicylidene)ethane-1,2-diamine] and that spontaneous oxidation of dinuclear (pc)Mn–CN–M′ species leads to [Cp(dppe)Fe–CN–Mn(pc)–O–Mn(pc)–NC–Fe(dppe)-Cp] **21**[91] containing a fully linear backbone keeping the two iron centres 13.2 Å apart.

Condensed aggregates

The non-terminal M–CN constituents of the chain-like complexes are difunctional which provides them with the possibility of becoming members of rings or one-dimensional polymers. But just like the longer chains, the rings are still rare for this type of compound (for the one-dimensional polymers, see below). The first ring-shaped trimer, $[(Ph_3P)(B_9C_2H_{11})Rh-CN]_3$ **22**,[92] was reported in 1982, and only two related trimetal rings with palladium[93] and samarium[94] have followed. Similarly, only one tetrametal ring, $[Cp_2Ti-CN]_4$ **23**,[95] has been proved by a structure determination while the constitution of the R_2AuCN tetramers rests mostly on molecular weight determinations.[96] At this point it is worth mentioning the unusual $Pd_4Mn_4(CN)_4$ complex **24** (Cp′ = η^5-C_5H_4Me) of Braunstein *et al.*[90] containing two intertwined $Pd_4Mn_2(CN)_2$ rings. This molecule, the topology of which can be derived from that of bis(noradamantane) (tricyclo[3.3.0.0^{3,7}]octane), is the finest example of chemical beauty in this article.

The simplest way of constructing aggregates of cyanometal units is the attachment of several metallocyanides to a central metal ion. This has been done in various ways, starting with the complex $[Hg\{NC-Co(NH_3)_5\}_4]^{10+}$ **25**[54] in 1964. A few partly cyanometallated complexes like $[(thf)_3Cr\{NC-Cr(CO)_5\}_3]$ **26**[97] (thf = tetrahydrofuran) followed.[25,51,97,98] Only quite recently has it become popular to build stars like $[Cr\{CN-Ni(tetren)\}_6]^{9+}$ **27**[99] (tetren = tetraethylenepentaamine) and $[Fe\{CN-Cu(tpa)\}_6]^{8+}$ **28**[100] [tpa = tris(2-pyridylmethyl)amine] combining central and peripheral redox-active metal centers.[100–102] In terms of ingenuity of design and beauty they all follow Fehlhammer and co-workers[102] star of stars **29** with M = Si, Ge, Sn and Cr.

The cyanometal aggregates with the highest number of metal atoms were not obtained by cyanide linking alone but by attaching cyanometal units as ligands to clusters. The first examples of this were derived from metal carbonyl clusters,[103–105] examples being $[HRu_3(CO)_{10}\{NC-Mn(CO)_2Cp\}_2]$ **30**[103] and $[\{Ru_3(CO)_{11}(\mu\text{-}CN)\}_2]^{2-}$ **31**.[104] Even higher nuclearities, culminating at 12, were achieved utilizing purely inorganic cluster cores, as in $[Fe_4S_4\{NC-Cr(CO)_5\}_4]^{2-}$ **32**[106] and $[Mo_6Cl_8\{NC-Mn(CO)_2Cp\}_6]^{2-}$ **33**.[107,108] This way the redox-active nature of the clusters and the cyanometal units can be combined, sometimes resulting in unusual magnetic properties.

One-dimensional polymers

If one wants to exploit the property of the cyanide link to transmit electronic effects one either has to link two functional units by a cyanometal chain (*i.e.* for light harvesting) or to produce ordered arrays of linear cyanometal polymers (*i.e.* for electric conductance). The latter, in simple terms, means the synthesis of one-dimensional polymers comprised of $[L_nM-CN]_x$ chains. So far this has been found not to be easy, neither in terms of designed synthesis of the polymers nor in terms of the crystallization of soluble L_nM-CN complexes as chain-like coordination polymers. In contrast there is an ever-growing number of two- and three-dimensional polymeric materials held together by M–CN–M′ links, culminating again in Prussian Blue and its analogues.

So far three approaches have been found to produce one-dimensional polymers with $[M-CN]_x$ backbones. Of these the most straightforward one seems to be the most difficult one too: the synthesis of L_nM-CN complexes with one open coordination site and the ability to stack one upon the other creating the infinite $[L_nM-CN]$ chains. Hanack and co-workers[109–113] have put much effort into this approach using porphyrin or phthalocyanine metal cyanides as building blocks. Polymers like $[(pc)Co-CN]_x$ **34** were obtained with Cr, Mn, Fe, Co and Rh as central metals and conductivities of up to 10^{-2} S cm^{-1} were achieved. A comparably simple approach involves the crystallization of one and the same compound, copper(I) cyanide with (mostly nitrogen) donor ligands.[114–117] When this is successful, the resulting crystals contain $[Cu-CN]_x$ zigzag chains as found in $[(py)Cu-CN]_x$ **35**[116] with three- or four-coordinate copper. The basic compound for this type of structure is $NaCu(CN)_2$.[118] As far as we know, electric conductivities of these compounds have not been determined yet.

In our opinion the most promising approach to obtain crystalline materials with linear chains of M–CN–M′ units is the combination of ionic metallocyanides with strictly *trans* oriented $M(CN)_2$ subunits and complex counter ions offering two coordination sites which are again reliably *trans* oriented, *e.g.* by bearing in-plane chelate ligands. Surprisingly we found only three examples for this with X-ray structural proof in the literature.[119–121] Two of them, $[(en)_2Ni-NC-Pd(CN)_2-CN]_\infty$ **36**[119] (en = ethane-1,2-diamine) and $[(H_2O)_4Mn-NC-Fe(CN)_4-CN]^-_\infty$ **37**,[120] contain the expected linear arrangements of M′–NC–M–CN fragments.

Structural and Physical Properties

The promise and challenge of oligonuclear metallocyanides is their ability to facilitate long-range electron transfer. The major part of the literature about them describes scientific work related to that. Several of the review articles[28,29,34–37,66,68,69] have 'application oriented' titles. But, alas, also in this field the number of catch phrases far exceeds the number of usable devices or even the number of new scientific ideas. Much is left to be done, and a more humble approach would be appropriate here and there.

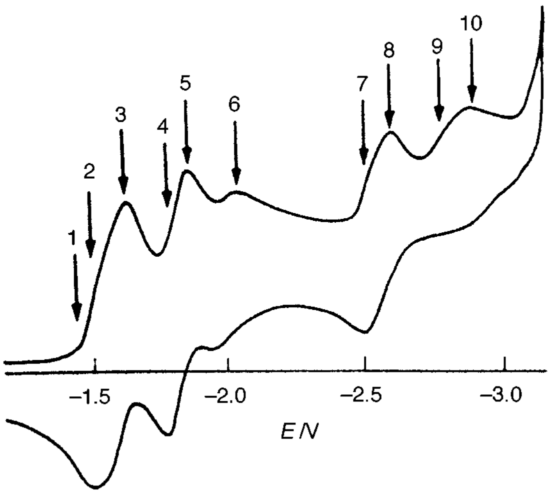


Fig. 1 Cyclic voltammogram of complex **16b** (reproduced with permission from ref. 73)

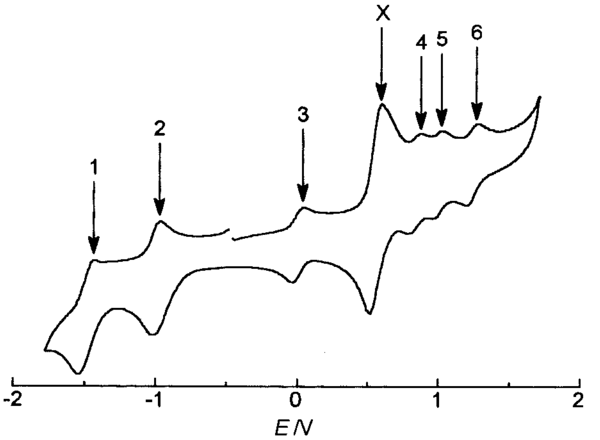


Fig. 2 Cyclic voltammogram of complex **21** (reproduced with permission from ref. 91). The wave marked X corresponds to the oxidation of co-crystallized Cp(dppe)Fe–CN

The most thoroughly investigated property is the response to irradiation with light (metal-to-metal charge transfer and metal-to-ligand charge transfer) in the context of charge mobility and mixed valence phenomena. Closely related to that are the investigations on the redox potentials and the electrochemical behaviour of the complexes. Both optical and redox behaviour are expressions of the electronic energies of the individual metallic components which are mediated by the cyanide links. Accordingly the ν(CN) wavenumbers are the third piece of information on the flow of electron density across the bridging cyanide ligands. The original papers and the review articles discuss the results of these measurements and their interrelations in great detail, and we refrain from repeating this discussion. Instead we want to focus on some more recent results and some more specific topics.

Redox phenomena

Oligonuclear metallocyanides can only show intramolecular charge transfer when they contain redox-active metal–ligand units. Their redox behaviour in solution, recorded as cyclic voltammograms, yields the basic corresponding information. The observed cyclic voltammograms may be surprisingly simple, *viz.* just one redox wave for $[(CN)_5Fe{-}CN{-}Pt(NH_3)_4{-}NC{-}Fe(CN)_5]^{4-}$.[20] They will show just a few waves even for tri- and tetra-nuclear complexes when these contain simple and isolated redox centers.[25,52,89] But they will be rich when the L_nM constituents bear ligands which are redox-active themselves, typically bipyridyl, catechol or phthalocyanine.[36,61,67,73,122] Extreme examples are presented in Figs. 1 and 2 for oligonuclear species with a high number of both redox-active metals and ligands.

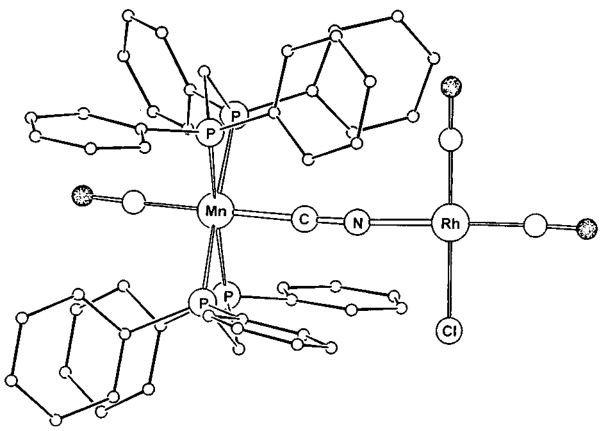


Fig. 3 Average shape of the structures of **38** and **38**$^+$

Table 1 Comparison of critical bond lengths (Å) and angles (°) for complexes **6a** and **6a**$^+$

	6a	**6a**$^+$
Cr–C (CN)	2.064(5)	1.998(11)
C–N	1.158(7)	1.135(11)
N–Fe	1.935(4)	1.892(8)
Cr–C (CO-*trans*)	1.84(1)	1.87(2)
Fe–P (ave.)	2.201(1)	2.259(3)
Cr–C–N	170.7(4)	173.1(9)
C–N–Fe	169.8(4)	165.2(8)

Table 2 Comparison of critical bond lengths (Å) and angles (°) for complexes **38** and **38**$^+$

	38	**38**$^+$
Mn–C (CN)	1.976(4)	1.964(6)
C–N	1.154(5)	1.148(7)
N–Rh	2.043(4)	2.038(5)
Mn–C (CO-*trans*)	1.776(4)	1.805(6)
Mn–P (ave.)	2.284(1)	2.352(2)
Rh–Cl	2.354(1)	2.340(2)
Rh–C (CO-*trans*)	1.838(6)	1.836(8)
Mn–C–N	178.5(4)	178.2(5)
C–N–Rh	176.9(4)	175.0(5)

In some cases it has been possible to prepare and isolate the oligonuclear complexes in two or three different states of oxidation (see the work by Connelly,[24] Bignozzi[67,73] and ourselves[45,53]) and thereby compare their photophysical and spectroscopic properties. We think that it is worthwhile to obtain more of such redox pairs or triplets, in order to put the interpretation of electrochemical or spectroscopic data on a firmer basis and to allow further-reaching comparisons. One important aspect of this would be the comparison of theoretical calculations with spectroscopic or structural data. As an example Fig. 3 and Tables 1 and 2 give structural information enabling a study of the only two pairs of redox isomers so far to have been subjected to an X-ray analysis, **6a**–**6a**$^+$ (ref. 45) and **38**–**38**$^+$ {$[(CO)(dppm)_2Mn{-}CN{-}Rh(CO)_2Cl]$ **38**} [dppm = bis(diphenylphosphino)methane] (ref. 82).

The main observation in both cases is that the structures of the neutral and monocationic complexes can be practically superimposed. The geometrical variations in the molecular cores (M–C, C–N, N–M′ bonds, M–C–N and C–N–M′ angles) are negligible for **38**–**38**$^+$, but appreciable for **6a**–**6a**$^+$ (oxidation causes bond shortening). The most noticeable features concern the metal–ligand bonds on the phosphine-bearing organometallic unit (Fe in **6a** and Mn in **38**) which are significantly lengthened due to reduced back bonding after oxidation. Thus

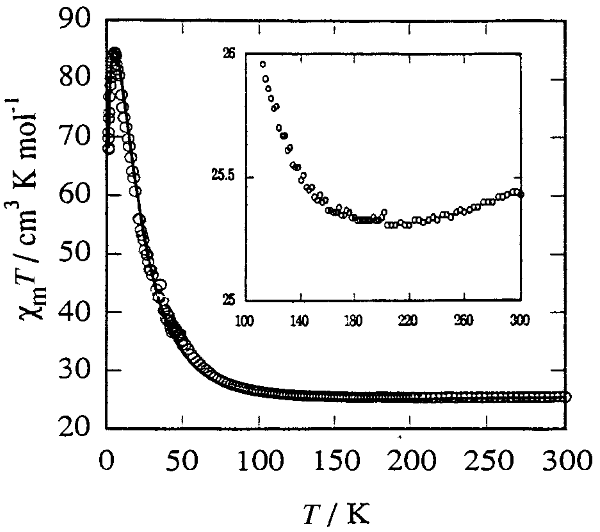


Fig. 4 Molar susceptibility of complex **42** (reproduced with permission from ref. 101)

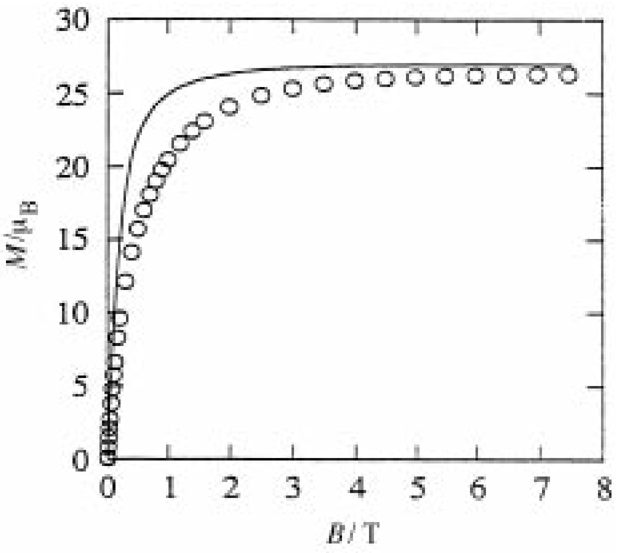


Fig. 5 Magnetization at $T = 2$ K for complex **42** (reproduced with permission from ref. 101)

the structural data support the statement that in these dinuclear complexes the phosphine-bearing unit is being oxidized but the cyanide ligand distributes and mediates the structural effects brought about by the oxidation.

Another approach to calibrating the various physical properties is the investigation of a series of oligonuclear compounds in which the nature of one of the constituents varies while the rest of the molecule remains unchanged. The simplest way of achieving this is to alter the electron density of one constituent in a given complex by subjecting it to varying solvation. Thus near-to-linear relations between solvent donor number and metal–metal charge-transfer (MMCT) energies could be found for dinuclear complexes having a $Cp(R_3P)_2M$ unit (M = Fe, Ru or Os) as one constituent,[45,123] and likewise such a relation with the solvent acceptor number was observed for a trinuclear $PtFe_2$ complex.[20] Similarly an increase in MMCT energy was seen when the ligand L in $[L(H_3N)_4Ru^{III}{-}NC{-}Fe^{II}(CN)_5]^-$ was made a stronger donor.[124]

The most common approach to this type of referencing is the comparison of redox potentials and MMCT energies.[20,76,80,125] As long as the redox step can be associated with just one constituent of the oligonuclear complexes or suitable corrections can be applied good linear fits between $E_{\frac{1}{2}}$ and ν(MMCT) are observed. A good example for this is the series of complexes $[(H_3N)_4Pt\{NC{-}Fe(CN)_4L\}_2]^{2-}$ with varying L.[76] It should be noted, however, that this is a simplistic approach, its success depends on favourable circumstances, and in many cases there are no linear relations between series of $E_{\frac{1}{2}}$ and ν(MMCT) values. Nevertheless it is a necessity to find more and better relationships of this kind in order to establish more general and systematic principles for the design and application of the polynuclear metallocyanides.

Molecular magnetism

Solid-state materials containing two- or three-dimensional arrays of cyanide bridged metal complex units enjoy a high degree of popularity because of their magnetic properties,[7] and several recent reviews have directed attention to them.[30,35] Surprisingly the molecular basis for this, in the form of magnetic interactions between a small number of metal atoms in oligonuclear complexes, has gained very little attention. We think that it deserves more, that it will produce as many surprises as the corresponding solid-state work, and that it will eventually provide a better understanding of the design and the properties of cyanometal-based magnetic materials.

For dinuclear complexes with one cyanide bridge there seem to be just a handful of magnetic measurements which have been interpreted. Typically they involve the metal ions Fe^{III} and Cu^{II}.[126–129] The magnetic interactions observed, however, span the whole range between strongly antiferromagnetic ($J = -88$ cm^{-1} for a Cu_2 complex[127]) and weakly ferromagnetic ($J = +0.25$ cm^{-1} for a FeCu complex[129]). Two typical examples are compounds $[H_3N(CN)_4Fe{-}CN{-}Fe(CN)_5]^{4-}$ **39** ($J \approx -27$ cm^{-1})[128] and $[(phen)_2Cu{-}CN{-}Cu(phen)_2]^{3+}$ **40** ($J = -29$ cm^{-1}).[127]

Very recently the star-like $M(CN{-}M')_n$ complexes (see above) have been designed specifically for magnetic studies, and each of the three measurements reported so far has yielded fascinating results. The tetranuclear complex $[(NC)_3Cr\{CN{-}Cu(edma)\}_3]$ **41**[99] (edma = ethylenediaminemonoacetate) shows weak magnetic coupling between Cr^{III} and Cu^{II} which is ferromagnetic at higher and antiferromagnetic at lower temperatures. Complex **27** is a very high spin system with a $S = \frac{15}{2}$ ground state and ferromagnetic coupling ($J = +17$ cm^{-1}) between Cr^{III} and Ni^{II}.[99]

The present record in terms of unpaired electrons has been set with $[Cr\{CN{-}Mn(tpen)\}_6]^{9+}$ **42**[101] [tpen = *N*,*N*,*N*′-tris(2-pyridylmethyl)-*N*′-methyl(ethane-1,2-diamine)]. It shows an antiferromagnetic coupling ($J = -8$ cm^{-1}) between Cr^{III} and Mn^{II} and a $S = \frac{27}{2}$ ground state. Its molar susceptibility and magnetization curves are shown in Figs. 4 and 5.

Consequences of cyanide–isocyanide isomerism

Since cyanide is not a symmetrical bridging ligand, turning it around will have a significant influence on the electronic situation of the two ML_n units attached to it. Conversely the two ML_n units, according to their donor and acceptor properties, will have different preferences for either the carbon (*i.e.* the acceptor) or the nitrogen (*i.e.* the donor) terminus of CN. This can be seen from the spontaneous isomerizations of complexes like **8**–**10**[19,49,52,53] or the equilibrations in solution of complexes like **7**[47,51] mentioned above. The simple expectation that in the more stable isomers the cyanide carbon is bound to the more electron-rich (more precisely better π donating) metal atom is borne out (though not to a full extent) by the examples given.

The infrared data for the ν(CN) vibration should yield similar information. However, as the strength of the C≡N bond responds to both the σ acceptor properties of the N-bound metal and the π donor properties of the C-bound metal, single pairs of isomers[42,43,47,49,51] may give conflicting results in terms of an increase or decrease of ν(CN) upon isomerization. The picture becomes more consistent if one compares series of isomer pairs, as can be seen in Table 3 for complex **6** and the

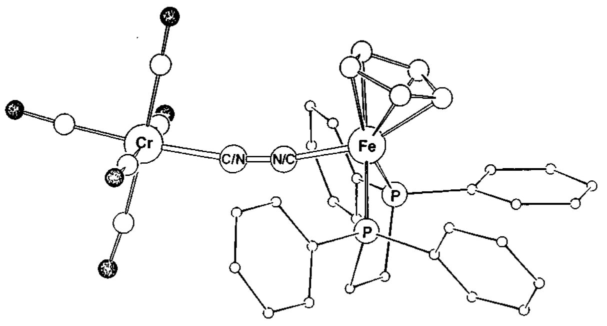


Fig. 6 Average shape of the structures of **6a** and **6b**

Table 3 The ν(CN) IR bands (cm^{-1}) and $E_{\frac{1}{2}}$ (ox) values (V against Ag–AgCl, in CH_2Cl_2) for pairs of cyanide–isocyanide isomers

	ν(CN)		$E_{\frac{1}{2}}$	
	Isomer **a**	Isomer **b**	Isomer **a**	Isomer **b**
6	2115	2103	+0.28	+0.46
43	2130	2157	+0.80	+0.68
44	2132	2151	—	—
45	2147	2094	+0.02	+0.24
46	2105	2087	+0.18	±0.00

Table 4 Comparison of critical bond lengths (Å) and angles (°) for the two pairs of cyanide–isocyanide isomers **5** [M = $(H_3N)_5Co$, M′ = Co-$(CN)_5$] and **6** [M = $(OC)_5Cr$, M′ = Fe(dppe)Cp]

	Complex **5**		Complex **6**	
	Isomer **a**	Isomer **b**	Isomer **a**	Isomer **b**
M–C/M–N	1.898(5)	1.921(4)	2.064(5)	2.086(3)
M′–N/M′–C	1.956(5)	1.886(4)	1.035(4)	1.897(4)
C–N	1.118(7)	1.152(5)	1.158(7)	1.151(5)
M–C–N/M–N–C	165.6(7)	159.8(3)	170.7(4)	165.1(3)
M′–N–C/M′–C–N	166.5(7)	172.4(3)	169.8(4)	174.3(4)

following complexes: [$(OC)_5$CrRFe$(CO)_2$Cp] (R = μ-CN **43a**, R = μ-NC **43b**), [$(OC)_5$WRFe$(CO)_2$Cp] (R = μ-CN **44a**, R = μ-NC **44b**), [Cp$(OC)_2$FeRMn$(CO)_2$Cp] (R = μ-CN **45a**, R = μ-NC **45b**) and [Cp(dppe)FeRMn$(CO)_2$Cp] (R = μ-CN **46a**, R = μ-NC **46b**).[45] The IR data in Table 3 follow the general trends discussed previously in a general context[22,27,33,70,86] and for specific examples.[21,24,107] First, the most electron-rich species [*i.e.* the complexes containing Cp$(OC)_2$Mn or Cp(dppe)Fe] show the lowest ν(CN) values. Secondly, within the pairs the one which has the cyanide carbon attached to the more electron-rich unit has the lower ν(CN). Thereby a structural assignment of the isomers can be made which agrees with that expected from the synthetic pathway.

Table 3 also lists the redox potentials for the first oxidation step of the complexes. For a given pair of isomers, that with the more electron-rich organometallic unit bound to nitrogen is 0.1–0.2 V easier to oxidize than the other one. This is in line with the σ donor and π acceptor properties of the cyanide ligand, and it can serve to identify which organometallic unit is being oxidized. Likewise, among the series of organometallic complexes related to those in Table 3,[45] only those containing the very electron-rich and substitution-inert Cp(dppe)Fe unit attached to the cyanide nitrogen could be isolated as stable compounds after one-electron oxidation. This in turn qualifies the individual organometallic units in the dinuclear complexes as rather independent and only weakly coupled electronically to each other, thereby causing localized redox changes.

A structural comparison of cyanide and iosocyanide bridged complexes was possible for the two pairs of compounds **5**[130,131] and **6**.[45,46] Both pairs are isostructural and in both cases the two individual molecular structures are practically superimposable. Fig. 6 shows this for the isomers **6a** and **6b**, and Table 4 lists the important structural features of the two pairs of complexes. It is noticeable that in all cases a metal–nitrogen bond is longer than the related metal–carbon bond (*e.g.* Cr–N in **6b** *vs.* Cr–C in **6a**) although the standard radius of nitrogen is smaller than that of carbon. This is in accord with the general observation for this type of complex that M–C π bonding is significant while M–N π bonding is not [*cf.* the discussion of ν(CN) data]. The same reason seems to account for the deviation from linearity of the M–N–C angles, being larger than those of the M–C–N angles, *i.e.* the 'linearizing' effect of M–C π bonding works more efficiently against the 'bending' effect of polar or packing interactions. The variation of the C≡N bond lengths between the four compounds is, as usual, too small to be discussed. Altogether these structural comparisons, just like those between the pairs of redox isomers **6a** and **38**, demonstrate the smoothing out of electronic imbalances by the bridging cyanide ligands.

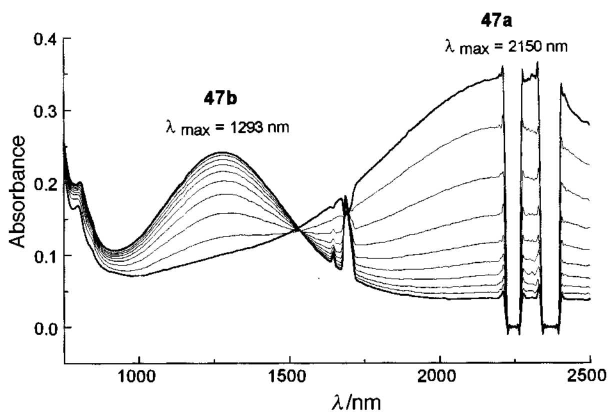


Fig. 7 The NIR spectra recorded during isomerization of **47a** to **47b** in dichloromethane solution. The three breakdowns in the spectral traces are artefacts caused by the spectrometer

One of the most attractive features of oligonuclear metallocyanides, the optically induced metal–metal charge transfer giving rise to the intervalence transfer (IT) bands in their UV/VIS/NIR spectra, has not been studied in detail with respect to cyanide–isocyanide isomerism. We did not find any examples of this for dinuclear complexes in the literature. One published case for trinuclear systems demonstrates, however, that a considerable change in the IT energy can result when the cyanide bridge is turned around: complex **8a** after a one-electron oxidation yields an IT band at 780 nm while the corresponding band for **8b** occurs at 1360 nm.[52] We made a similar observation for the two isomers [(pc)Fe{(μ-CN)Fe(dppe)Cp}$_2$]$^+$ **47a** and [(pc)Fe{(μ-NC)Fe(dppe)Cp}$_2$]$^+$ **47b**. Fig. 7 shows the spectral traces recorded during the spontaneous and clean isomerization of **47a** to **47b** in solution.[53] It is obvious that such pronounced phenomena deserve further study.

In terms of the application of oligonuclear metallocyanides as conductors for electron transfer the orientation of the cyanide linkages may be an important factor for the direction and ease of electron flow. An example of the different efficiency of two linkage isomers when used as sensitizers fixed to TiO_2 underlines this.[50] And in the same context it is interesting to note that there seem to be just two cases so far of trinuclear complexes, namely **10b**[53] and **12**,[72] which contain both CN bridges oriented in the same direction.

Long-range interactions

In order to fulfil the promise of oligonuclear metallocyanides, long-range interactions, *i.e.* those between the end groups of a cyano-bridged metal chain, must be found and exploited. This has not been easy so far because most of the trinuclear complexes reported are symmetrical, possessing a M(CN–M′)$_2$ or M(NC–M′)$_2$ arrangement with two identical end groups linked in the same way to the central metal atom. One standard approach of detecting an electronic communication between the two end groups, the recording of intervalence transfer bands in the electronic spectra, is normally impossible for these compounds because the IT takes place between the central and the terminal groups. It could, however, be shown that the long-range IT transitions occur in the NIR region for those trinuclear complexes which are unsymmetrical. This was the case for **11** ($\lambda = 1220$ nm)[62] and for the corresponding bis-$Ru(NH_3)_5$ complex after reducing one of the $Ru^{III}(NH_3)_5$ entities to the Ru^{II} state ($\lambda = 1050$ nm).[60] A complete spectral analysis revealed that rather weak long-range IT bands can also be observed in some of the symmetrical trinuclear complexes with central $Ru(bipy)_2$ units.[26,62] For the unsymmetrical trinuclear complex **12** resonance-Raman spectroscopy was applied to identify the radiation-induced end-to-end charge transfer.[72] A similar transfer was assumed for the related tetra- and penta-nuclear complexes with $ReRu_n$ chains.[37,72]

The most common way of identifying long-range interactions between the terminal metal units in symmetrical trinuclear complexes has been cyclic voltammetry. In those cases where the two terminal metal units are the first to be oxidized or reduced, and hence it is easy to identify the corresponding redox waves, a splitting of the redox wave will demonstrate that after a one-electron transfer one of those two units 'knows' of the redox change of the other. Conversely, if a two-electron transfer occurs at one and the same potential the two terminal redox centers do not communicate. The latter has been observed for trinuclear complexes with central $[Pt(NH_3)_4]^{2+}$,[20,132] Ag^+, and Cu^+[24] units. Weak to intermediate communication was indicated by a noticeable splitting of the redox waves for complexes $[Au\{NC{-}Mn(CO)_2P(OR)_3(dppm)\}_2]^+$ **48**[24] and $[(CO)_2Rh\{NC{-}Mn(CO)_2PR_3(dppm)\}_2]^+$ **49**.[82]

The two couples of *cis–trans* complexes **16** and **17** (see above) have allowed the influence of the orientation of the two terminal cyanometal units on their electronic interaction to be assessed. As expected, this is stronger for a *trans* arrangement, *i.e.* a linear $M_3(CN)_2$ chain. While *cis*-**17b** shows a single two-electron transfer, *trans*-**17a** displays a splitting of the redox wave by 100 mV.[88] The effect is more pronounced for the couple *cis*-**16b** ($\Delta E = 80$ mV)[61] and *trans*-**16a** ($\Delta E = 280$ mV),[21] which must, however, be considered with care as the two compounds **16a** and **16b** are not real isomers. The electrochemical investigation of the linear tetranuclear complex **21**[91] (see Fig. 2) has lent support to the expectation that electronic interaction along a straight chain of M–CN units should be strong. The redox waves observed at 0.81 and 0.98 V in benzene–acetonitrile (3:1) are assigned to one-electron oxidations of the terminal FeCp(dppe) units. Their separation of 0.17 V identifies the interaction between these two units which are 13.2 Å apart as medium to strong.

Consequences of Metal–Metal Charge Transfer

In the preceding paragraphs the ability of the chain-like metallocyanides to conduct electronic charge has been viewed from varying standpoints. The question that now has to be answered is whether there is, or can be, a practical use of this property in terms of electrical conductance or chemical consequences of charge separation. As usual, this is much more difficult to achieve, and consequently this section will be much shorter than the previous ones.

Unidirectional electron transfer

The basic phenomenon of metal–metal charge transfer across a cyanide bridge which manifests itself in the IT bands in the electronic spectra is well-investigated, see the listing of review articles. Its observation as a long-range charge transfer across two or three consecutive cyanide bridges is already limited to a few cases, see the preceding section. Among these, only unsymmetrical complexes like **11** and **12** have the potential for unidirectional charge transfer, generating a mobile electron (or hole) by charge separation at one end of the chain and delivering it to the other end. Accordingly, these complexes have been discussed repeatedly in connection with light harvesting, antenna sensitizers, energy transfer, photovoltaic cells, supramolecular devices, *etc.*[28,30,34,36,37,52,66,68,69] Until now, however, none of the complexes has found a real practical application.

The device which was most often investigated in this respect is the wide-bandgap semiconductor TiO_2 treated with metallocyanides as sensitizers.[37,65,77] Quite satisfying photocurrent efficiencies were observed. While it is doubtful that there is end-to-end charge transfer in the trinuclear metallocyanides employed, it is worth mentioning that the pair of Re–CN–Ru cyanide–isocyanide isomers used[50] show different behaviour as sensitizers.

Electrical conductance through an oligonuclear metallocyanide, *e.g.* by using it as a coating for electrodes, has, to our knowledge, not been observed yet. There is no doubt that it is possible as Hanack and co-workers[109,113] have shown that one-dimensional polymers with linear $(M{-}CN)_x$ backbones can have quite high electrical conductivities.

Photoredox reactions

The light-induced metal–metal charge transfer changes the oxidation states of at least two metal ions in an oligonuclear metallocyanide. If the metal ions in these new oxidation states are substitutionally labile and/or thermodynamically preferred the oligonuclear complex may fall apart yielding the product mixture of a redox disproportionation.[29] In some simple cases where the synthesis of the oligonuclear complexes was a redox reaction itself this amounts to a photolytic regeneration of the starting materials. Such is the case for the irradiation of complexes $[(CN)_5Co^{III}{-}NC{-}Fe^{II}(CN)_5]^{6-}$ **50** {generating $[Co^{II}(CN)_5]^{3-}$ and $[Fe^{III}(CN)_6]^{3-}$}[133] and $[(H_3N)_4Pt^{IV}\{NC{-}Fe^{II}(CN)_5\}_2]^{4-}$ **51** {generating $[Fe^{III}(CN)_6]^{3-}$ and $[Pt^{II}(NH_3)_4]^{2+}$}.[76,132]

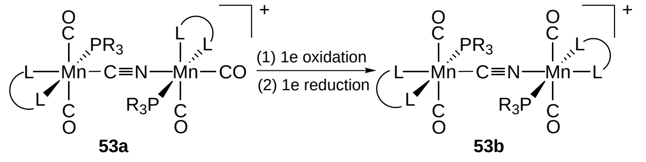
In other cases the initial products of the photoredox reaction contain units which are highly labile as mononuclear complexes and thus can escape from the charge-transfer generated intermediate by ligand substitution, thereby leading to fragmentation and decomposition of the oligonuclear metallocyanide. This was observed for the $Co^{III}Co^{III}Ru^{II}$ complex **13** decomposing to Co^{II} and cyano complexes of Co^{III} and Ru^{III},[57] as well as for the $Ru^{III}Ru^{II}Co^{III}$ complex **14** decomposing to Co^{II} and complexes of Ru^{III}.[58]

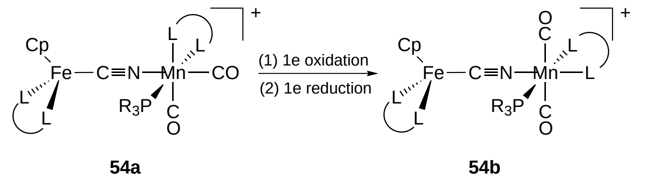
A reaction type which is common in other fields of photochemistry, the radical attack on solvents by photoredox-generated odd-electron species, seems to have been observed in only one case so far for oligonuclear metallocyanides. The intermediate Ti^{III} species produced by the photolytic disproportionation of $[Cp_2Ti^{IV}\{NC{-}Ru^{II}(CN)_5\}_2]^{6-}$ **52** {producing $[Ru^{III}(CN)_6]^{3-}$ as the by-product} attacks the solvent $CHCl_3$ and abstracts a chlorine atom regenerating the Ti^{IV} state.[134]

Remote chemical reactions

What the chemist would like to see as a result of the 'communicative' properties of the bridging cyanide ligand are chemical changes at one end of the metallocyanide chain induced by an event happening at the other end. The primary event might be a light-induced excitation, a redox reaction or a ligand substitution. There are many ways to envisage such remote chemical reactions, but to our knowledge only one type has been observed so far. So just like the possible application of metallocyanides in electrochemical devices, this possibility is more a wish than a reality so far.

The reaction type that has been found is remote isomerization. It was observed for the *cis* ⟶ *trans* rearrangement of





$Mn(CO)_2(PR_3)(L–L)$ units in dinuclear complexes (L–L = chelating diphosphine). Carriedo and co-workers[135,136] found several such isomerizations after oxidations of the complexes containing *cis*-$Mn(CO)_2(PR_3)(L–L)$ at one end. The cases of **53**[135] and **54**[136] are shown as examples. The primary oxidation occurs at the *trans* configured manganese center on the left side of **53a** and at the iron center of **54a**. Subsequently an electron transfer across the cyanide bridge takes place creating a Mn^{II} center on the right side of the complexes which undergoes *cis* $\longrightarrow$ *trans* isomerization. The oxidized and isomerised species **53b** (ox) and **54b** (ox) are stable as such, but can subsequently be reduced to **53b** and **54b** maintaining the *trans* configuration at the manganese centers.

Conclusion

This article was meant to direct attention to the chemical and structural diversity and some of the elementary physical and chemical properties of the oligonuclear metallocyanides. It draws its justification from basic research and curiosity rather than from application and optimization. Accordingly the emphasis of the presentation was more on compounds, structures, and properties related thereto and not so much on spectroscopy, electrochemistry and photophysics.

It is obvious that there is an enormous range of ways in which cyanometal units can be linked to one another, thus creating equally many ways of electronic communication between metal centers. So far the investigation of this communication is mostly limited to interactions across single cyanide bridges. Therefore in our opinion the real challenge of the chemistry and physics of oligonuclear metallocyanides has yet to be met: the design, preparation and study of complexes with appreciable and chemically and physically productive long-range interactions.

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