Chain-Like Tetra-, Penta- and Heptanuclear Cyanide-Bridged Complexes by Attachment of Organometallic Cyanides to M_2, M_3 and M_5 Units

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Attachment of the "ligands" [Cp(dppe)Fe-CN], [Cp(PPh_3)$_2$-Ru-CN], [Cp(CO)$_2$Fe-CN] and [(CO)$_5$M-CN]$^-$, (where M = Cr, Mo, W) to the polymetallic centres [Ru_2(OAc)$_4$]$^+$, [Co_3(dpa)$_4$]$^{2+}$ and [Ni_5(tdpa)$_4$]$^{2+}$ yielded two tetra-, three penta- and five heptanuclear complexes with chain-like linear arrangements of the metal ions and the bridging cyanide ligands, as proved by the structure determination of [Ni_5(tdpa)$_4${Cp(dppe)$_2$Fe-CN}$_2$](PF_6)$_2$. IR and CV data show that the Ru_2, Co_3 and Ni_5 centres of these complexes withdraw electron density from the external organometallic units. This prevents electronic interactions between the two terminal metal ions, yet allows multistep one- and two-electron redox processes.

Introduction

Molecular wires, comprised of arrays of metal atoms surrounded by ligands as insulators, are attractive as conducting leads in nanoscale devices, with possible applications ranging from electrical connections to light harvesting antennas.[1−3] One approach to the design of such wires is the lining up of metals and bridging ligands up to infinite arrays, as was successfully applied to metal-cyanide combinations.[3−5] The other approach is direct linking of the metal atoms along the chain, as applied successfully in the Krogmann salts.[6]

Well-defined molecular species of this kind, with nanoscale dimensions, have not been prepared yet. The longest $(M\text{-}CN)_x$ chain which has been crystallographically characterised contains seven manganese atoms.[7] Likewise, the longest chain-like array with metal-metal bonds is formed from seven chromium atoms.[8] Like others,[5] we are involved in attempts to stretch these limits.

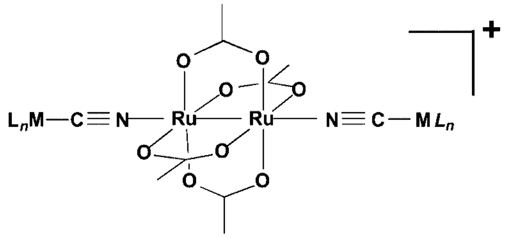
Our contributions to this field have so far consisted in the synthesis and investigation of $(M\text{-}CN)_x$ arrays.[9−14] We were able to show that there exist electronic interactions between terminal metals as far as 12 Å apart[9] and that a 90° angle in a chain interrupts such interactions.[11] We also observed the drawback that with increasing length the $(M\text{-}CN)_x$ chains become fragile, showing a tendency for dismutation with formation of shorter fragments.

Following on from here, it seemed favourable to us to combine the advantages of the cyanometal building blocks (i.e. a large variability) with those of the metal-metal bonded chains (i.e. rigidity due to their rigid ligand environment). This paper reports on some combinations of Ru_2, Co_3 and Ni_5 chains with terminal organometallic cyanides. Other than us[15] only the group of Kühn has prepared related complexes based on [Re_2(OAc)$_4$][16] and [Mo_2(OAc)$_4$] units.[17]

Results and Discussion

Derivatives of [Ru_2(OAc)$_4$]$^+$

The [Ru_2(OAc)$_4$]$^+$ unit is a mixed-valence species containing Ru^{II} and Ru^{III}. This is promising in terms of redox chemistry, particularly when combined with the redox chemistry of cyanide-linked metal complex units. We therefore attached the organometallic cyanides [Cp(dppe)Fe-CN] and [Cp(PPh_3)$_2$Ru-CN] to this core by reacting them with [Ru_2(OAc)$_4$(THF)$_2$]BF_4. The complex cations **1a** and **1b** were obtained as tetrafluoroborate salts.



1a: L_nM = Cp(dppe)Fe **1b:** L_nM = Cp(PPh_3)$_2$Ru

Confirmation of the identity of complexes **1a** and **1b** was obtained independently by an X-ray analysis of **1b** as a hexafluoroantimonate salt.[15] Information on their electronic nature can be drawn from the ν(CN) values in their

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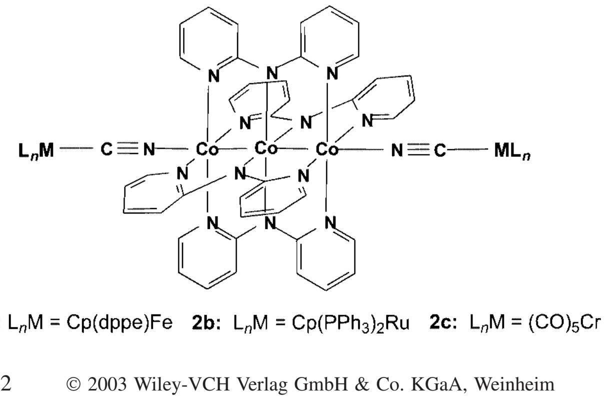
IR spectra. The corresponding bands (2059 cm^{-1} for **1a** and 2061 cm^{-1} for **1b**) are lower by 3 and 10 cm^{-1}, respectively, than those in the free L_nM-CN "ligands". Previously, we observed that ν(CN) is raised in similar situations, reflecting the kinematic effect, i.e. the increased energy for the CN vibration due to the attachment of CN^- to two metal centres.[11–13] However, for dinuclear CN-bridged complexes we had also observed that ν(CN) can be lowered when the metal centre attached at the N terminus is strongly electron-withdrawing.[18] In those cases the electron withdrawal is compensated by increased M→C π-back-donation from the other metal centre, which populates antibonding orbitals and lowers the strength of the C–N bond. Complexes **1** seem to represent an intermediate situation, where the kinematic effect and the back-bonding effect are virtually identical. The important conclusion from this is that the Ru_2 core is an electron sink which may impede electronic interactions between the two terminal metal centres.

This is also evident from the electrochemical investigation of **1a** and **1b**. The electrochemical response of the Ru_2 core of these complexes is poor, as is that of the parent complexes $[Ru_2Cl(RCOO)_4]$,[19] showing only an irreversible reduction around −0.4 V (in CH_2Cl_2 vs. Ag/AgCl). The oxidative waves assigned to the organometallic cyanides occur at +0.67 V for **1a** and +1.02 V for **1b**. Both these values are 0.2 V higher than those of the free organometallic cyanides. This confirms the electron withdrawal by the Ru_2 core, which, by means of the π-back-donation, extends to the terminal metal centres. The electrochemical waves have the characteristics of reversible one-electron transfers. Together with the notion that there is no splitting of the redox waves, this indicates that there is no electronic interaction between the two terminal iron or ruthenium atoms. The same observation was made by Kühn for the related complexes with Re_2 and Mo_2 cores.[16,17]

Derivatives of $[Co_3(dpa)_4]^{2+}$

Complexes with metal chains stabilized by sawtooth-like pyridylamide ligands were introduced by Peng.[8,20,21] To start with we chose the best-investigated example with the shortest chain length, i.e. the cobalt(II) complex.[22,23] The reactions between $[Co_3(dpa)_4]Cl_2$ and the cyanometal complexes [Cp(dppe)Fe-CN], $[Cp(PPh_3)_2Ru\text{-}CN]$ and Na-$[(CO)_5Cr\text{-}CN]$ were straightforward and yielded the pentanuclear complexes **2a–c**. Complexes **2a** and **2b** are dications and were isolated as hexafluoroantimonate salts. Complex **2c** is neutral.



2a: L_nM = Cp(dppe)Fe **2b**: $L_nM = Cp(PPh_3)_2Ru$ **2c**: $L_nM = (CO)_5Cr$

Complexes **2a–c** could not be obtained in the form of crystals suitable for X-ray analysis, yet their identity is evident from their spectra and their redox behaviour. The ν(CN) band-positions of **2a** and **2b** (2055 and 2057 cm^{-1}) are virtually identical to those of **1a** and **1b**. The slight lowering of the ν(CN) values relative to those of the free organometallic cyanides leads to the same conclusions as above: the $[Co_3(dpa)_4]^{2+}$ core, just like the $[Ru_2(OAc)_4]^+$ core, seems to be a rather strong electron acceptor. The fact that the ν(CN) band of **2c** (2120 cm^{-1}) is raised by 17 cm^{-1} with respect to that of free $[(CO)_5Cr\text{-}CN]^-$ is not in contradiction with this conclusion: upon formation of the pentanuclear complex the negative charge of $[(CO)_5Cr\text{-}CN]^-$ disappears, hence the strong Cr→C π-back-donation is diminished and this results in a strengthening of the C–N bond.

The electrochemical behaviour of complexes **2** underlines the strong electron-acceptor properties of their $[Co_3(dpa)_4]^{2+}$ cores (see Table 1 and Figure 1). The first oxidative wave corresponds to a one-electron oxidation of the Co_3 unit. The second wave represents the transfer of two electrons, one each from the two terminal metal atoms. Relative to free $[Co_3(dpa)_4(CH_3CN)_2]^{2+}$ the Co_3 core in complexes **2** is easier to oxidize by 0.1–0.2 V, reflecting the electron donation from the organometallic cyanides, typically strongest from the anionic $[(CO)_5Cr\text{-}CN]^-$. In turn, the terminal metal units are more difficult to oxidize by roughly 0.4 V, in comparison to the free organometallic cyanides. This is about twice as much as in complexes **1**, indicating that the Co_3 unit is a stronger electron acceptor than the Ru_2 unit. As above, the redox wave for the organometallic cyanides is not split into two components, again indicat-

Table 1. Cyclovoltammetric data (in CH_2Cl_2, potentials in V vs. Ag/AgCl) of complexes **2** and their reference compounds

	$E_{1/2}(1)$	$E_{1/2}(2)$
[Cp(dppe)Fe-CN]		0.48
$[Cp(PPh_3)_2Ru\text{-}CN]$		0.79
$[(CO)_5Cr\text{-}CN]^-$		0.58
$[Co_3(dpa)_4(CH_3CN)_2]^{2+}$	0.60	
2a	0.46	0.83
2b	0.51	1.25(irr)
2c	0.40	0.93

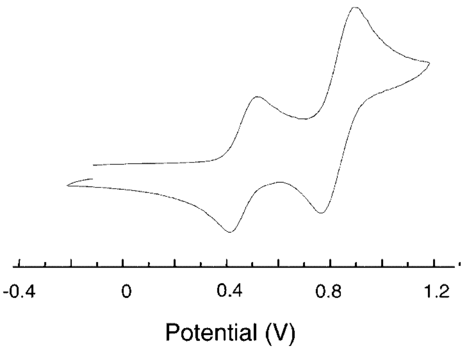


Figure 1. Cyclic voltammogram of **2a** (in CH_2Cl_2, potentials vs. Ag/AgCl)

ing that the central polymetallic unit interrupts electronic communication between the two terminal metal atoms.

The electronic spectra of complexes **2** (for details see Exp. Sect.) are very similar to those of the Co_3 parent compounds $[Co_3(dpa)_4]Cl_2$ and $[Co_3(dpa)_4(CH_3CN)_2](PF_6)_2$.[22,23] Very strong absorptions in the near UV and one strong absorption in the visible range can be assigned to π-π* and MLCT transitions, and very weak absorptions in the NIR to d-d transitions of the Co^{II} ions. Complexes **2** show no additional features other than a slight intensification of the NIR bands. The positions of the NIR bands of **2a** and **2b** make it clear that they are not MMCT bands representing electron transfer from the outer metal centres to the Co_3 core: the prominent band for the Ru complex **2b** at 1248 nm occurs at lower energy by 26 nm than the corresponding band for the Fe complex **2a** at 1222 nm. Yet $[Cp(PPh_3)_2Ru\text{-}CN]$ is much more difficult to oxidize than [Cp(dppe)Fe-CN] (see Table 1). Hence these band positions only reflect the influence of the terminal organometallic units on the electronic structure of the Co_3 core.

The reversible redox steps in the cyclic voltammograms indicate that complexes **2** should be suitable for chemical oxidations. This was probed for **2a**. Addition of one equivalent of magic blue [$(4\text{-Br-}C_6H_4)_3N^+$ as the SbF_6 salt, $E_{1/2} = +1.0$ V[24]] produced a change of colour and spectra, addition of two further equivalents produced another. The resulting complex cations which we assign as **2a′** and **2a′′** were stable enough to be investigated in solution, but we failed to isolate them as pure complex salts.

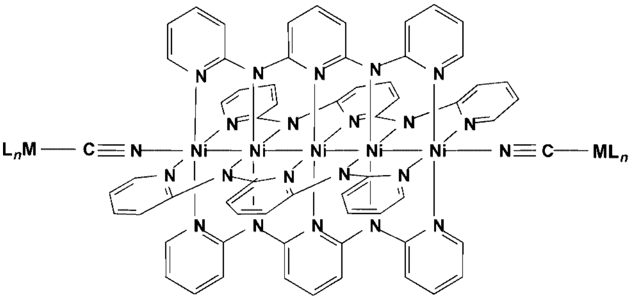
$[Cp(dppe)Fe\text{-}CN\text{-}Co_3(dpa)_4\text{-}NC\text{-}Fe(dppe)Cp]^y$

2a: $y = 2+$, **2a′**: $y = 3+$, **2a"**: $y = 5+$

The ν(CN) bands in the IR spectra of **2a**, **2a′** and **2a′′** occur at 2057, 2047 and 2134 cm^{-1}, respectively, in CH_2Cl_2 solution. The changes are in agreement with the structural and electronic assignments given above. The decrease from **2a** to **2a′** reflects the increased charge on the Co_3 core and hence its increased electron withdrawal. The sharp rise from **2a′** to **2a′′** reflects the positive charges on the two terminal Cp(dppe)Fe units, which dramatically reduces their ability for M→C π-back-donation. In the electronic spectrum of **2a′** (for details see Exp. Sect.) two new bands of medium intensity occur in the far visible and near IR range. In the electronic spectrum of **2a′′** these two new bands are shifted to lower energies. New bands of similar position and intensity were also observed upon one-electron oxidation of $[Co_3(dpa)_4]Cl_2$.[25] The simplest interpretation is that they are due to MMCT transitions within the $Co^{II}_2Co^{III}$ core. There is no obvious relation in terms of MMCT with the terminal [FeCp(dppe)] units, other than the band shift upon changing their oxidation state. Thus, similar to the situation with the $[Ru_2(OAc)_4]$-derived complexes, neither the electrochemical behaviour nor the electronic spectroscopy of complexes **2** indicate any electron transfer behaviour, be it between the two terminal metal units or between one of these units and the trimetal core.

Derivatives of $[Ni_5(tpda)_4]^{2+}$

The starting material for our heptanuclear complexes, $[Ni_5Cl_2(tpda)_4]$, was also described for the first time by Peng.[20] After conversion to its more reactive form, $[Ni_5(tpda)_4(CH_3CN)_2]^{2+}$, by reaction with $AgBF_4$ in acetonitrile,[26] it could be reacted with [Cp(dppe)Fe-CN], $[Cp(PPh_3)_2Ru\text{-}CN]$, $[Cp(CO)_2Fe\text{-}CN]$, $Na[(CO)_5Mo\text{-}CN]$ and $Na[(CO)_5W\text{-}CN]$. Complexes **3a−e** resulted in moderate yields. They were isolated as deeply coloured crystalline hexafluorophosphate salts (**3a**, **3b**, **3c**) or neutral complexes (**3d**, **3e**).



3a: L_nM = Cp(dppe)Fe **3b:** $L_nM = Cp(PPh_3)_2Ru$ **3c:** $L_nM = Cp(CO)_2Fe$

3d: $L_nM = (CO)_5Mo$ **3e:** $L_nM = (CO)_5W$

Crystals of **3a** were chosen for a representative structure determination (see Figure 2). The complex cation has internal symmetry, with the central nickel atom being located on a twofold axis. The central molecular axis of **3a** which is comprised of 11 atoms (5 Ni, 2 Fe, 2 CN) is almost perfectly linear, with the strongest bending occurring typically at the nitrogen atom of the bridging cyanide (172°). The helical nature of the $[Ni_5(tdpa)_4]$ core, due to the wrapping of the tdpa ligands, and the uneven distribution of Ni−Ni distances along the Ni_5 chain closely correspond to those in the parent complexes, $[Ni_5Cl_2(tpda)_4]$[20] and $[Ni_5(tpda)_4(CH_3CN)_2](PF_6)_2$.[26] The geometry of the [Cp(dppe)Fe-CN] "ligands" compares well with that in related di- and trinuclear complexes.[9−14,18] Neither the Fe−C nor the C−N distances in all the cyanide-bridged complexes derived from [Cp(dppe)Fe-CN] vary so much as to draw reliable conclusions on the amount of Fe→C π-back-donation. Thus, the structural data of such oligometallic complexes yield no information about the net electron withdrawal from the terminal organometallic cyanides to the central M_2, M_3 or M_5 core. The two iron atoms in **3a** are 19.4 Å apart, which is the longest distance between such terminal redox centres in cyanide-bridged complexes observed so far.

As for complexes **1** and **2**, the IR data of complexes **3** yield unambiguous information on the net electron withdrawal from the terminal organometallic cyanides into the Ni_5 core. Table 2 shows that this is the same as in **1** and **2** for **3a** and **3b** [slight lowering of ν(CN)] as well as for **3d** and **3e** [slight increase of ν(CN)]. Complex **3c** shows a large increase in ν(CN) as compared to free $[Cp(CO)_2Fe\text{-}CN]$. This clearly supports the notion that in all the other complexes described here, it is the M→C π-back-donation

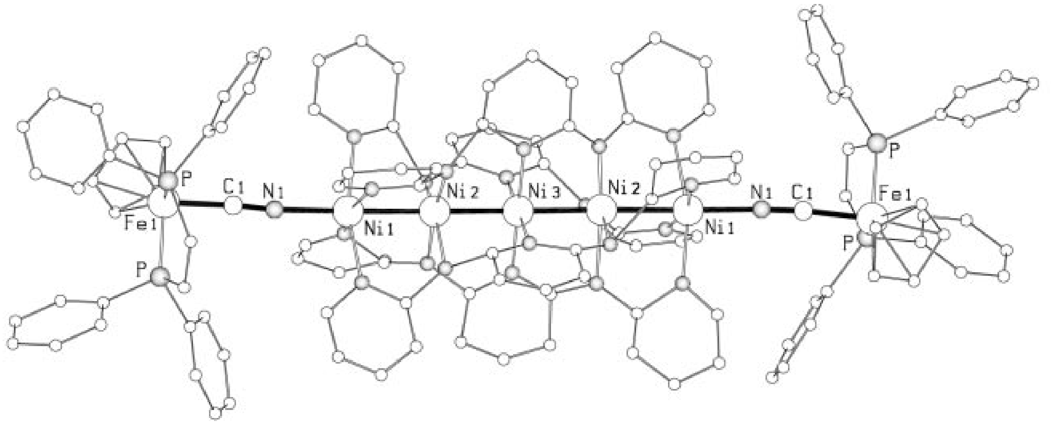


Figure 2. Molecular structure of the complex cation of **3a**; relevant bond lengths (Å) and angles (°): Ni1−Ni2 2.384(1), Ni2−Ni3 2.306(1), Ni1−N1 2.021(6), N1−C1 1.14(1), C1−Fe1 1.882(7); Fe1−C1−N1 175.4(2), C1−N1−Ni1 172.3(1), N1−Ni1−Ni2 178.7(1), Ni1−Ni2−Ni3 178.8(1), Ni2−Ni3−Ni2′ 180

Table 2. ν(CN) Data of complexes **3** and reference compounds

	Complex	Free L_nM-CN
3a	2062	2062
3b	2067	2072
3c	2141	2106
3d	2116	2107
3e	2120	2111

which provides the electron flow from the terminal metal units to the M_n complex cores: [Cp(CO)$_2$Fe-CN] is quite electron-poor compared to [Cp(dppe)Fe-CN] (its redox potential is more than 1 V higher), and hence it can provide much less electron density for π-back-donation. Thus, the kinematic effect is the decisive influence on ν(CN) of **3c**, resulting in a rather high ν(CN) value.

The redox behaviour of complexes **3a−c** is mostly that of their Ni_5 core (see Table 3). The reference complex $[Ni_5(tdpa)_4]^{2+}$ undergoes a reversible one-electron oxidation and can be isolated in the form of $[Ni_5(tdpa)_4]^{3+}$ compounds.[27] As we found for $[Ni_5(tdpa)_4(CH_3CN)_2]^{2+}$, there are two further irreversible oxidation steps. Complexes **3a−c** also show these three redox steps, albeit in ill-resolved, yet reversible, cyclic voltammograms. Figure 3 shows this in the case of **3a**, which is the only complex **3** that also displays the redox wave for the organometallic cyanide.

In the cyclic voltammogram of **3a** the redox wave assigned as $E_{1/2}(2)$ is twice as high and hence must be associated with the oxidation of the two [FeCp(dppe)] units present. If this is so, then **3a** compares favourably with **2a**: in both cases the redox potential of the organometallic cyanide is raised by 0.2−0.3 V while that of the Co_3 or Ni_5 core is lowered by ca. 0.2 V. This clearly reproduces the conclusions on the net flow of electron density drawn from the IR data. Complexes **3b** and **3c** do not give such a clear indication of the electronic situation. Their organometallic cyanides are more difficult to oxidize. This results in a lesser effect on the first redox potential of the Ni_5 unit and hides their redox waves in the cyclic voltammograms. Again, as before for **1a** and **2a**, there is no splitting of the redox wave due to the [FeCp(dppe)] unit in **3a**. Furthermore, attempts at chemical one-electron oxidation of **3a** (which was shown to be possible for the parent Ni_5 complex[27]) were not successful.

Table 3. Cyclovoltammetric data (in CH_2Cl_2, potentials in V vs. Ag/AgCl) for complexes **3** and the Ni_5 reference compound

	$E_{1/2}(1)$	$E_{1/2}(2)$	$E_{1/2}(3)$	$E_{1/2}(4)$
3a	0.44	0.72	1.11	1.31
3b	---	0.67	1.10	1.28
3c	---	0.68	1.08	1.26
$[Ni_5(tpda)_4(CH_3CN)_2](PF_6)_2$		0.68	0.94(irr)	1.29(irr)

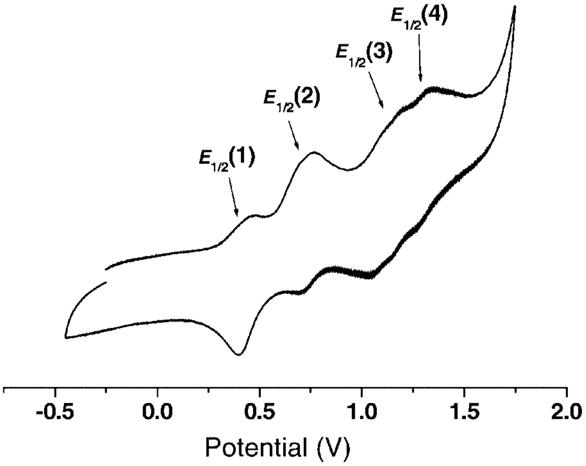


Figure 3. Cyclic voltammogram of **3a** (in CH_2Cl_2, potentials vs. Ag/AgCl)

The UV/Vis spectra of complexes **3** (for details see Exp. Sect.) only show the features of their Ni_5 core. The absorptions due to the organometallic cyanides are completely hidden. There are intense π-π* and MLCT transitions up to about 400 nm and weak d-d bands in the 500−700 nm range.[26] Upon one-electron oxidation of $[Ni_5Cl_2(tpda)_4]$

MMCT bands show up in the NIR.[27] The spectra of complexes **3** show no features of this kind which might be attributed to a MMCT from the electron-rich organometllic units to the electron-poor Ni_5 core. Actually the spectrum of **3a**, which, due to its easily oxidizable [FeCp(dppe)] constituents, should be most suitable for such a MMCT, is virtually superimposable to that of $[Ni_5(tpda)_4Cl_2]$.

Conclusions

The concept of constructing cyanide-bridged extended arrays of metal ions by linking organometallic cyanides to chain-like polymetallic units was applied successfully. Tetra-, penta- and heptanuclear complexes based on Ru_2, Co_3 and Ni_5 cores were obtained. The pronounced electron-acceptor properties of the core units result in a stable attachment of the terminal cyanometal constituents. The structure determination of **3a** with an almost perfectly linear Fe-CN-Ni_5-NC-Fe array and an Fe−Fe distance of 19.4 Å has confirmed the longest distance between two such Cp(dppe)Fe-CN units yet.

The spectroscopic data of the new complexes have shown uniformly that their Ru_2, Co_3 and Ni_5 cores are electron sinks. They withdraw electron density from the terminal organometallic units via the CN bridges, yet not to an extent that optically induced MMCT occurs. For all three complex types the first oxidative process converts one of the metal ions in the core from the M^{II} to the M^{III} state. This further increases the electron-sink properties of the core units. As a result any possible MMCT between the two terminal organometallic units is interrupted, and MMCT occurs either within the core units or from one of the terminal units into the core.

One goal of this work, i.e. finding electronic communication between the terminal units in complexes with longer chain lengths, could not be achieved. Both the electron-sink properties of the core units and the failure to observe split redox waves for [FeCp(dppe)] and related units prevented this. It has been achieved in much longer chains with electronically more balanced (e.g. polyacetylide) chains,[28] leaving the challenge to find similarly suitable chains in cyanide-bridged systems.

Experimental Section

General: The general experimental and measuring techniques are given in ref.[11]. $[Ru_2(OAc)_4(THF)_2]BF_4$,[29] $[Co_3(dpa)_4]Cl_2$,[22] $[Ni_5(tpda)_4(CH_3CN)_2](BF_4)_2$,[26] [Cp(dppe)Fe-CN],[30] $[Cp(PPh_3)_2$-Ru-CN],[30] $[Cp(CO)_2$Fe-CN][31] and $Na[(CO)_5$M-CN] with M = Cr, Mo, W[32] were prepared according to the published procedures.

1a: [Cp(dppe)Fe-CN] (30 mg, 0.06 mmol) was added with stirring to a solution of $[Ru_2(OAc)_4(THF)_2]BF_4$ (20 mg, 0.03 mmol) in 10 mL of THF. After 2 h the solvent was removed in vacuo and the residue dissolved in 10 mL of dichloromethane. Layering with hexane led, within a few days, to the separation of 25 mg (50%) of **1a** as blue-green crystals. M.p. 330 °C (dec.). $C_{72}H_{70}BF_4Fe_2N_2O_8P_4Ru_2$ (1615.89): calcd. C 53.52, H 4.37, N 1.73; found C 52.91, H 4.28, N 1.64.

1b: Like **1a** from $[Cp(PPh_3)_2$Ru-CN] (170 mg, 0.20 mmol) and $[Ru_2(OAc)_4(THF)_2]BF_4$ (80 mg, 0.10 mmol). Yield 100 mg (50%) of **1b** as red-brown crystals. M.p. 174 °C. $C_{92}H_{82}BF_4N_2O_8P_4Ru_4\cdot 2CH_2Cl_2$ (1958.65 + 169.87): calcd. C 53.04, H 4.07, N 1.32; found C 52.81, H 4.04, N 1.13.

2a: A mixture of $[Co_3(dpa)_4]Cl_2$ (102 mg, 0.09 mmol) and [Cp(dppe)Fe-CN] (101 mg, 0.19 mmol) in 40 mL of ethanol and 20 mL of dichloromethane was treated with $NaSbF_6$ (48 mg, 0.19 mmol) and stirred for 1 h. After filtration the solvents were removed in vacuo. The residue was extracted with 20 mL of dichloromethane and the extract layered with 60 mL of hexane. Within a few days 135 mg (60%) of **2a** had separated as brown crystals. M.p. 223 °C. $C_{104}H_{90}Co_3F_{12}Fe_2N_{14}P_4Sb_2$ (2419.81): calcd. C 51.62, H 3.75, N 8.10; found C 51.07, H 3.57, N 7.93. UV/Vis (CH_2Cl_2): λ (ε) = 404sh (19000), 430sh (10500), 460sh (2100), 560 (3600), 1222 nm (240).

2b: Like **2a** from $[Co_3(dpa)_4]Cl_2$ (85 mg, 0.08 mmol), $[Cp(PPh_3)_2$Ru-CN] (114 mg, 0.16 mmol) and $NaSbF_6$ (41 mg, 0.16 mmol). Yield 92 mg (43%) of **2b** as brown crystals. M.p. 240 °C. $C_{124}H_{102}Co_3F_{12}N_{14}P_4Ru_2Sb_2$ (2762.57): calcd. C 53.91, H 3.72, N 7.10; found C 53.93, H 2.78, N 7.20. UV/Vis (CH_2Cl_2): λ (ε) = 396sh (17000), 452sh (5800), 512sh (1500), 526 (2800), 1248 nm (190).

2c: Like **2a** from $[Co_3(dpa)_4]Cl_2$ (79 mg, 0.07 mmol) and $Na[(CO)_5$Cr-CN] (35 mg, 0.15 mmol) in 50 mL of ethanol. Yield 50 mg (57%) of **2c** as a red powder. M.p. 184 °C. $C_{52}H_{32}Co_3Cr_2N_{14}O_{10}$ (1293.70): calcd. C 48.28, H 2.49, N 15.16; found C 48.05, H 2.43, N 14.10. UV/Vis (CH_2Cl_2): λ (ε) = 394 (13500), 458sh (5200), 510sh (1550), 558 (2830), 1194 nm (300).

Chemical Oxidation of 2a: A 0.1 M solution of $[(4\text{-Br-}C_6H_4)_3N]SbF_6$ [24] in CH_2Cl_2 was added dropwise with stirring to a 0.1 M solution of **2a** in CH_2Cl_2. IR spectroscopy indicated the formation of **2a′** after addition of one molar equivalent and the formation of **2a′′** after the addition of two further molar equivalents, as evident from their ν(CN) bands at 2047 and 2134 cm^{-1}, respectively. UV/Vis data: **2a′**: λ (ε) = 424 (8300), 582sh (3050), 712 (6900), 1096 (2300); **2a′′**: λ(ε) = 432 (10300), 546 (3200), 714 (3400), 1180 (1800), 1420 nm (1300).

3a: A solution of $[Ni_5Cl_2(tpda)_4]$ (42 mg, 0.03 mmol) and $AgBF_4$ (12 mg, 0.06 mmol) in 20 mL of dichloromethane and 4 mL of acetonitrile was stirred for 1 h. After removal of the solvents in vacuo the residue was extracted with 10 mL of dichloromethane and the extract filtered off. [Cp(dppe)Fe-CN] (33 mg, 0.06 mmol) was added to this solution. After 4 h of stirring, NH_4PF_6 (12 mg, 0.07 mmol) and 1 mL of methanol were added. After 10 min of stirring the solution was filtered off. Slow diffusion of diethyl ether into this solution yielded, within one week, 48 mg (63%) of **3a** as black crystals. M.p. 340 °C (dec.). These crystals, containing dichloromethane and methanol, were taken as such for the structure determination. Pumping in vacuo converted them into a solvent-free powder. $C_{124}H_{102}F_{12}Fe_2N_{22}Ni_5P_6$ (2719.28): calcd. C 54.77, H 3.78, N 11.33; found C 54.23, H 4.07, N 11.04. UV/Vis (CH_2Cl_2): λ (ε) = 368 (9400), 472 (640), 596 nm (880).

3b: Like **3a** from $[Ni_5(tpda)_4Cl_2]$ (56 mg, 0.04 mmol), $AgBF_4$ (16 mg, 0.08 mmol), $[Cp(PPh_3)_2$Ru-CN] (57 mg, 0.08 mmol) and NH_4PF_6 (15 mg, 0.09 mmol). Yield 32 mg (25%) of **3b** as black crystals. M.p. 320 °C (dec.). $C_{144}H_{114}F_{12}N_{22}Ni_5P_6Ru_2\cdot CH_2Cl_2$

(3070.11 + 84.93): calcd. C 55.34, H 3.72, N 9.79; found C 55.41, H 4.25, N 9.79. UV/Vis (CH_2Cl_2): λ (ε) = 364 (6800), 388 (6000), 482 (680), 536 (790), 600 nm (980).

3c: Like **3b** with [Cp(CO)$_2$Fe-CN] (16 mg, 0.08 mmol). Yield 31 mg (38%) of **3c** as black crystals. M.p. 340 °C (dec.). $C_{76}H_{54}F_{12}Fe_2N_{22}Ni_5O_4P_2$ (2034.48): calcd. C 44.87, H 2.68, N 15.15; found C 44.77, H 2.58, N 15.04. UV/Vis (CH_2Cl_2): λ (ε) = 360 (5100), 388 (4300), 492 (700), 548 (760), 606 nm (820).

3d: Like **3a** from [Ni$_5$(tpda)$_4$Cl$_2$] (56 mg, 0.04 mmol), $AgBF_4$ (16 mg, 0.08 mmol) and Na[(CO)$_5$Mo-CN] (23 mg, 0.08 mmol), without addition of NH_4PF_6. Yield 15 mg (20%) of **3d** as black crystals. M.p. 340 °C (dec.). $C_{72}H_{44}Mo_2N_{22}Ni_5O_{10}\cdot 0.5CH_2Cl_2$ (1870.64 +42.47): calcd. C 45.71, H 2.38, N 16.18; found C 45.53, H 2.49, N 15.53. UV/Vis (CH_2Cl_2): λ (ε) = 366 (2500), 376 (2300), 470 (170), 536 (200), 588 nm (250).

3e: Like **3d** with Na[(CO)$_5$W-CN] (30 mg, 0.08 mmol). Yield 11 mg (12%) of **3e** as black crystals. M.p. 340 °C (dec.). $C_{72}H_{44}N_{22}Ni_5O_{10}W_2\cdot 2CH_2Cl_2$ (2038.43 + 169.87): calcd. C 40.25, H 2.19, N 13.95; found C 40.56, H 2.32, N 13.80. UV/Vis (CH_2Cl_2): λ (ε) = 356 (10700), 394 (8700), 474 (1900), 534 (2400), 590 nm (2900).

Structure Determination:[33] The crystal of **3a** was taken directly from the reaction solution. Diffraction data were recorded at room temperature on a Bruker Smart CCD diffractometer and subjected to an empirical absorption correction. The structure was solved with direct methods and refined anisotropically with the SHELX program suite.[34] Hydrogen atoms were included with fixed distances and isotropic temperature factors 1.5 times those of their attached atoms. Parameters were refined against F^2. The R values are defined as $R_1 = \Sigma|F_o - F_c|/\Sigma F_o$ and $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]\Sigma[w(F_o^2)^2]\}^{1/2}$. Drawings were produced with SCHAKAL.[35] Table 4 lists the crystallographic data.

Table 4. Crystallographic data for complex **3a**

Empirical formula	$C_{127}H_{112}Cl_2F_{12}Fe_2N_{22}Ni_5O_2P_6$
Molecular mass	2868.36
Crystal size (mm)	0.25 × 0.25 × 0.10
Space group	$C2$
Z	2
a (Å)	20.852(7)
b (Å)	18.706(6)
c (Å)	18.727(6)
α (°)	90
β (°)	90.817(6)
γ (°)	90
V (Å^3)	7303(4)
D(calc) (gcm^{-3})	1.30
μ(Mo-K_α) (mm^{-1})	0.99
hkl range	h: −27 to 19 k: −23 to 25 l: −25 to 24
Measured reflections	22385
Independent reflections	14607
Observed refl. [$I > 2\sigma(I)$]	6545
Parameters	776
Refined reflections	14607
R_1 (obs.refl.)	0.090
wR_2 (all refl.)	0.320
Residual electron density (e/Å^3)	+1.2/-0.6

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