

Synthesis of Oligometallic Compounds from *tripod*Iron(II) Species Using Cyano Bridging Ligands – Electronic Coupling of Two Metal Termini Through Metal Dicyano and Diisocyano Entities

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Dedicated to Professor Henri Brunner on the occasion of his 66th birthday

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Organometallic monocyano-metalates $[M-CN]^-$ (**1**[−]) [$M = Cr(CO)_5$ **1a**[−], $Cr(\eta^6-CF_3C_6H_5)(CO)_2$ **1b**[−], $Mn(\eta^5-CH_3C_5H_4)(CO)_2$ **1c**[−]] produce tetrametallic (**2**[−]) and trimetallic (**3**) aggregates upon reaction with *tripod* and iron(II) salts [*tripod* = $CH_3C(CH_2PPh_2)_3$]. The tetranuclear compound [*tripod*Fe{NC-M}₃][−] (**2**[−]) [$M = Cr(CO)_5$] or the trinuclear species [*tripod*Fe(CO){NC-M}₂] (**3**) [$M = Cr(CO)_5$ **3a**, $Cr(\eta^6-CF_3C_6H_5)(CO)_2$ **3b**, $Mn(\eta^5-CH_3C_5H_4)(CO)_2$ **3c**] can be selectively formed by following the appropriate reaction protocols. Organometallic dicyano-metalates $[NC-M'-CN]^-$ (**4**[−]) [$M' = Mn(CO)_4$ **4a**[−], $CpFe(CO)$ **4b**[−], $CpCo(CN)$ **4c**[−]] react in a similar manner to give pentanuclear species [*tripod*Fe{NC-M'-CN}₃Fe*tripod*]⁺ (**5**⁺). – In compounds **2**[−] and **3**, two easily oxidizable organometallic groups are linked through a *tripod*Fe(NC)₂ unit, while in **5**⁺ two *tripod*iron(II) entities are linked through a less readily oxidizable $M'(CN)_2$ unit. For both types of compound, at least two distinct revers-

ible oxidations are observed by cyclic voltammetry. The potentials at which these oxidations occur are characteristic of the terminal groups in each case. The potentials of the two consecutive oxidation steps are separated by between 150 and 350 mV. The oxidation products of compounds **2**[−], **3**, and **5**⁺ can hence be classified as class III mixed-valence species with comproportionation constants K_C of between 10^2 and 10^6 . The extent of electronic coupling mediated by the $M'(CN)_2$ or $M'(NC)_2$ bridging entities is thus similar to that mediated by $[RC(CN)_2]^-$ bridging ligands in otherwise analogous compounds, for which K_C values of around 10^4 are observed. All the aforementioned compounds have been characterized by analytical and spectroscopic techniques, including cyclic voltammetry and UV/Vis spectroscopy. In addition, X-ray crystallographic data are reported for **2**[−], **3a**, **3b**, **3c**, and **5a**⁺.

Introduction

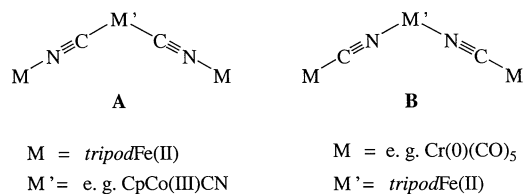
Dinitrile ligands are efficient building blocks for the synthesis of oligonuclear coordination compounds.^[1] Anionic geminal dinitrile ligands $[RC(CN)_2]^-$, $N(CN)_2^-$ have been found to lead to efficient electronic coupling between the terminal metal centers in the corresponding $M-NC-X-CN-M$ arrangements.^[2] It would appear that the nature of the linking unit X has little influence on the efficiency of this coupling, since the separation between the first and second oxidation potentials of the corresponding compounds is relatively constant, irrespective of the nature of X .^[2] Even the replacement of RC^- by N^- as X does not greatly affect this separation.^[2] The distance between the two metal centers in compounds of the type $M-NC-X-CN-M$ ($X = RC^-, N^-$) is around 700 pm, which is rather similar to the distance between two metal centers linked by *cis*-dicyano complexes $M'(CN)_2$.^[3] Compounds of this type have been extensively studied by Vahrenkamp,^[4] who showed that these inorganic bridging li-

gands are quite effective in mediating electronic coupling between the two terminal metal centers in an $M-(\mu-CN)-M'-(\mu-CN)-M$ arrangement.

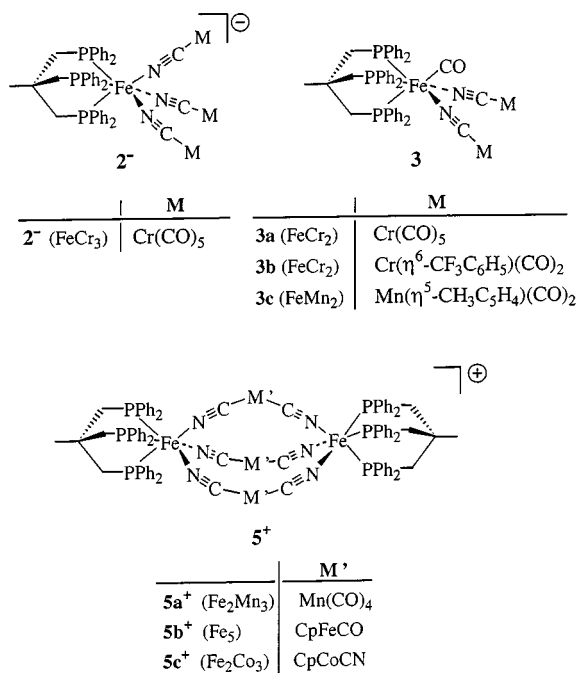
As the efficiency of electronic coupling is easily measured by cyclic voltammetry, and since the electrochemical behavior of dinuclear *tripod*iron compounds [*tripod* = $CH_3C(CH_2PPh_2)_3$] in which the two iron centers are linked through $X(CN)_2$ entities [$X = RC^-, N^-$] is well known,^[2] it was tempting to synthesize *tripod*iron derivatives having the two iron(II) centers linked by $M'(CN)_2$ bridging units (Scheme 1, A). We report herein the synthesis of such compounds (**5**⁺) and the measurement of their degree of electronic coupling. Moreover, *tripod*iron(II) templates may also serve to address the same type of problem in an inverted version. Compounds of the type [*tripod*FeL{NC-M}₂] contain the *tripod*Fe^{II}L unit in a central position (Scheme 1, B).

In these compounds, the terminal metal centers are bridged by a $CN-Fe-NC$ ligand entity. Cyclic voltammetry of such compounds should reveal the ability of this type of linker to electronically couple the two terminal metal centers. The synthesis of such compounds (**2**[−] and **3**; Scheme 2) and the efficiency of electronic coupling through the *tripod*Fe(NC)₂ linker are described herein.

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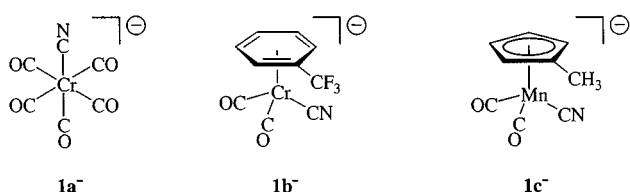
Scheme 1. Two types of inorganic groups linking two metal centers M



Scheme 2. The tripodiron compounds described in this paper

Results and Discussion

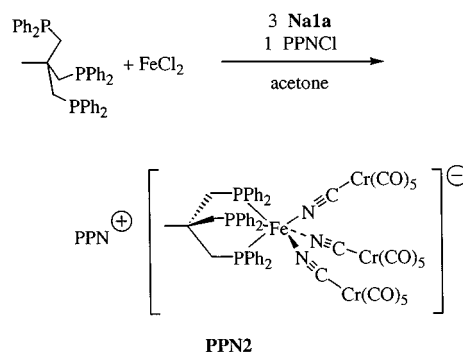
It has been shown that the N-termini of nitrile groups in organometallic cyano compounds are quite nucleophilic.^[5] The nucleophilicity of metal-bonded cyano groups has been known since the early days of organic chemistry.^[6] This appears to be a general property of anionic coordination compounds containing cyano ligands and has been amply demonstrated for species of type $\mathbf{1}^-$ by their reactions with main-group^[7] or transition-metal-centered^[8] electrophiles. Compounds $\mathbf{1a}^-$ and $\mathbf{1c}^-$ (Scheme 3) are easily accessible as their sodium or potassium salts by published procedures.^[9]

Scheme 3. Organometallic monocyanometalate ligands $\mathbf{1}^-$

Compound $\mathbf{1b}^-$ could be obtained by irradiation of the parent (arene)tricarbonyl species^[10] in methanol in the presence of excess potassium cyanide^[11] as its intensely orange-colored potassium salt. Its composition was unequivocally confirmed by its analytical and spectroscopic data (see Exp. Sect.).

$\mathbf{K1b}$ shows an irreversible oxidation wave in its cyclic voltammogram at $E_{\text{pa}} = -100$ mV (CH_3CN , vs. SCE). It is thus easily oxidized and is similar in this respect to $\mathbf{Na1a}$.^[12a] No data are available for $\mathbf{K1c}$ itself, but the parent compound $\text{Na}[\text{CpMn(CO)}_2\text{CN}]$ is reversibly oxidized at 40 mV vs. SCE^{[4][12b]} and the oxidation potential of $\mathbf{1c}^-$ can be expected to be of the same order. All compounds $\mathbf{1}^-$ are thus oxidized at much lower potentials than the tripodiron(II) entity in a coligand environment of nitrile groups. The oxidation of $[\text{tripodFe}(\text{CH}_3\text{CN})_3]^{2+}$ occurs at 1400 mV (CH_3CN , vs. SCE)^[13] and oxidation of this entity in the dinuclear compounds $[\text{tripodFe}\{\mu\text{-NC-C(R)-CN}\}_3\text{Fe}(\text{tripod})]^+$ requires a minimum of 900 mV vs. SCE.^[2c] This combination of facts makes compounds $\mathbf{1}^-$ ideal ligands for testing the electronic coupling properties of a tripodFe(NC)₂ unit linking two redox-active metal centers (Scheme 1, B).

The reaction of equimolar amounts of tripod and FeCl_2 with three equivalents of $\mathbf{Na1a}$ in acetone gives a red solution, from which, after cation exchange with PPNCl and crystallization, $\mathbf{PPN2} \cdot 0.75 \text{CH}_2\text{Cl}_2$ is obtained in the form of red needle-shaped crystals (Scheme 4).

Scheme 4. Synthesis of $\mathbf{PPN2}$

The constitution of the tetranuclear anion $\mathbf{2}^-$ was unequivocally proven by the spectroscopic and analytical data of $\mathbf{PPN2}$ (Table 2). The signals of the axial and equatorial carbonyl groups as well as of the nitrile groups are clearly resolved in the ^{13}C NMR spectrum of $\mathbf{PPN2}$ (Table 3), while its infrared spectrum shows weak bands attributable to ν_{CN} absorptions at 2126 cm^{-1} and 2135 cm^{-1} . The ν_{CO} band pattern (Table 2) is consistent with the presence of Cr(CO)_5 groups, although the pattern is somewhat more complicated than that generally observed for LCr(CO)_5 compounds with undisturbed local C_{4v} symmetry. This indicates some deviation of these groups from this local symmetry in the tetranuclear anion. The structure of $\mathbf{PPN2} \cdot 0.75 \text{CH}_2\text{Cl}_2$, as determined by single-crystal X-ray analysis (Figure 1; Tables 1 and 8), shows an overall close to C_3 -symmetric arrangement for the anion $\mathbf{2}^-$. The rotational

positions of the phenyl groups, as well as those of the $\text{Cr}(\text{CO})_5$ entities, are close to this idealized symmetry (Table 1; torsion angles τ , ϕ , and χ).

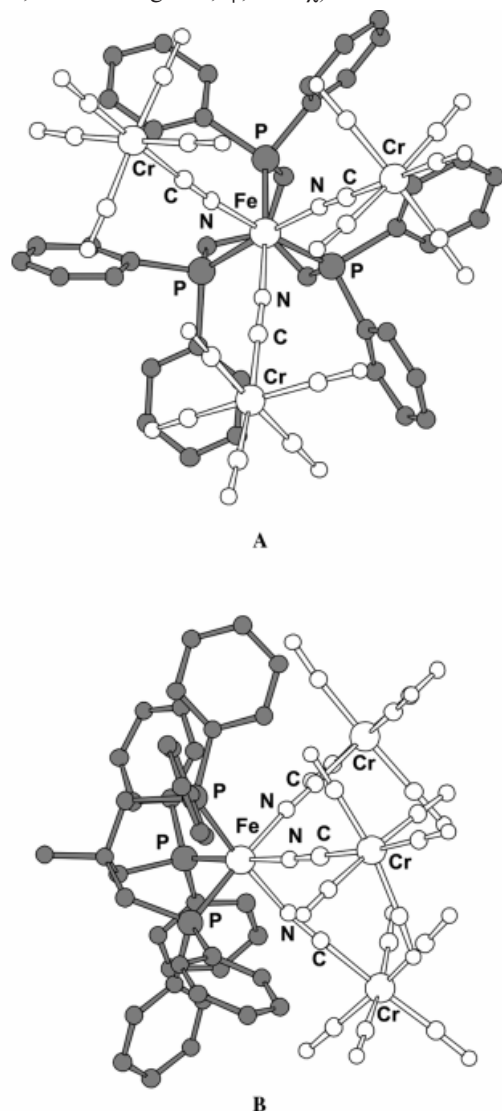


Figure 1. Two views of the structure of the tetranuclear anion 2^-

Short $\text{O}\cdots\text{H}$ contacts are seen between some of the equatorial carbonyl groups and the protons of the phenyl rings. Each pentacarbonylchromium group is involved in at least one such contact with $\text{H}\cdots\text{O}$ distances in the range 260–300 pm (Table 1). Even though this is not indicative of hydrogen bonding, it shows that the *tripod*iron entity and the $\text{Cr}(\text{CO})_5$ groups are in steric interference with one another. Disturbance of the local C_{4v} symmetry of the $\text{Cr}(\text{CO})_5$ groups, as inferred from the IR-spectroscopic data, is thus consistent with the observed structure.

When equimolar mixtures of *tripod* and FeCl_2 in acetone are treated with 2 equiv. of either **Na1a**, **K1b**, or **K1c**, or orange-red solutions result. On bubbling CO through these solutions, they undergo a color change to orange-brown.

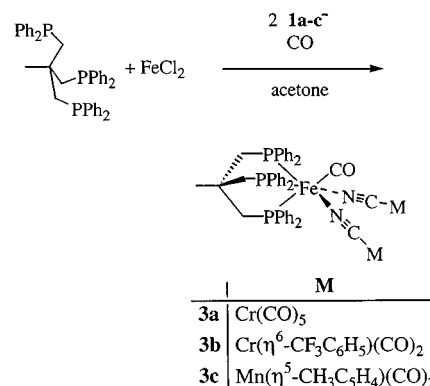
The trinuclear compounds **3** were isolated as red-brown crystalline materials in yields of around 80%. The identities

Table 1. Bond lengths and angles in the tetranuclear anion 2^-

Fe–P	225.3(2)–226.0(2) ^[a]	τ_1 ^[b]	35.5(4)
Fe–N	195.6(5)–197.7(5)	τ_2	32.6(4)
Cr–C _{CN}	203.5(7)–207.2(7)	τ_3	32.1(5)
Cr–C _{CO,ax}	185.1(7)–186.8(6)	ϕ_a ^[c] ^[d]	–36.4 to –68.5
Cr–C _{CO,eq}	188.9(7)–192.7(8)	ϕ_b	–13.7 to –19.9
Fe–N–C	170.2(4)–176.2(5)	χ_1 ^[e]	–67/23
Cr–C–N	177.6(5)–178.8(5)		–156/112
P–Fe–P	84.7(2)–87.3(2)	χ_2	–71/21
N–Fe–N	87.4(1)–91.1(6)	χ_3	–51/37
O $\cdots\text{H}$ ^[f]	262		–163/108
	266		–51/37
	277		–147/120

^[a] The values in parentheses are standard deviations in units of the last decimal listed. – ^[b] τ denotes the torsion angles Fe–P–C–C within the chelate cage. – ^[c] The suffixes a and b refer to the two classes of aryl groups, which would be equivalent under exact C_3 symmetry (Figure 1, A). – ^[d] ϕ designates a torsion angle $C_{\text{ortho}}-C_{\text{ipso}}-P-Hz$, where Hz is the end point of a vector vertical to the plane spanned by the three phosphorus nuclei and fixed to one phosphorus center, pointing in the direction of the observer with respect to Figure 1, A. – ^[e] χ denotes the torsional arrangement of the $\text{Cr}(\text{CO})_5$ groups. It is defined as the torsion angle $Hx-Fe-Cr-O_{\text{CO,eq}}$, where Hx is the end point of a vector radiating from the iron center along the idealized C_3 axis in a direction away from the observer with respect to Figure 1, A. – ^[f] Shortest distance between a carbonyl oxygen atom of any of the three pentacarbonylchromium units and a hydrogen atom of a *tripod* phenyl substituent.

of the compounds **3a**, **3b** (FeCr_2), and **3c** (FeMn_2) (Scheme 5) were unequivocally established from their spectroscopic data (Tables 2 and 3) and X-ray analyses (Tables 4 and 8; Figure 2).

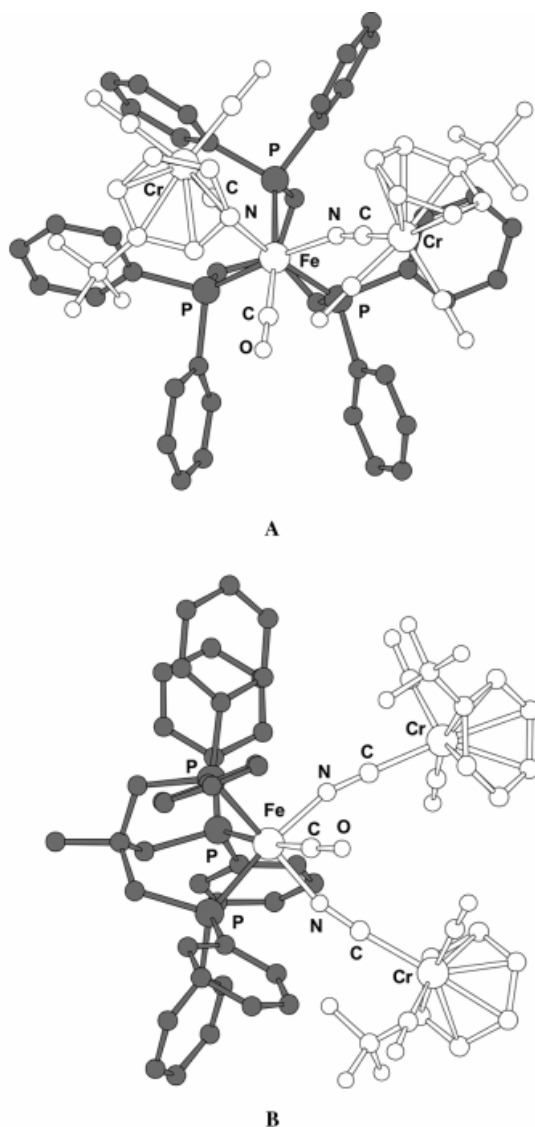


Scheme 5. Synthesis of compounds **3**

The infrared spectra of compounds **3** each feature a band at around 2030 cm^{-1} (Table 2), attributable to the iron-bonded carbonyl group. The ν_{CN} vibrations are observed as one band envelope at around 2100 cm^{-1} . The ν_{CO} vibrations of the $\text{Cr}(\text{CO})_5$ groups in **3a** produce the expected pattern (Table 2). The CO groups of the $\text{Cr}(\eta^6\text{-CF}_3\text{C}_6\text{H}_5)(\text{CO})_2$ entities in **3b** give rise to two bands of equal intensity, as do those of the $\text{Mn}(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)(\text{CO})_2$ entities in the FeMn_2 compound **3c** (Table 2). The ^{31}P NMR spectra of compounds **3** each show a doublet of higher intensity and a

Table 2. Spectroscopic and analytical data for compounds **PPN2** and **3**

No.	Formula (M [g/mol])	C _{calcd.} , H _{calcd.} , N _{calcd.} , P _{calcd.} C _{found} , H _{found} , N _{found} , P _{found}				IR (CH ₂ Cl ₂): $\tilde{\nu}$ [cm ⁻¹]			Yield (%)
						ν_{CN}	ν_{CO}		
PPN2	C ₉₅ H ₆₉ Cr ₃ FeN ₄ O ₁₅ P ₅ (1873.3)	60.91, 3.71, 2.99, 8.27 60.97, 3.93, 2.99, 8.10				–1336 [<i>tripod</i> Fe(1a) ₃] [–]	2135 w 2126 vw	2062 m 1938 vs 1887 vs	52
3a	C ₅₄ H ₃₉ Cr ₂ FeN ₂ O ₁₁ P ₃ (1144.5)	56.66, 3.43, 2.45, 8.12 56.63, 3.91, 2.43, 8.00				–	2123 w 2030 m	2061 m 1937 vs 1923 vs	80
3b	C ₆₂ H ₄₉ Cr ₂ F ₆ FeN ₂ O ₅ P ₃ (1268.8)	59.08, 3.85, 2.19, 7.25 58.80, 3.97, 2.25, 7.21				+ 960 [<i>tripod</i> Fe(1b) ⁺	2087 m 2024 w	1907 vs 1844 vs	84
3c	C ₆₀ H ₅₃ FeMn ₂ N ₂ O ₅ P ₃ (1140.7)	63.17, 4.68, 2.46 61.73, 4.79, 3.32				–	2089 m 2022 w	1917 vs 1851 vs	83

Figure 2. Two views of the structure of complex **3b**

triplet of lower intensity (Table 3). This is consistent with the static idealized octahedral coordination geometry around the iron centers, with two phosphorus nuclei lying *trans* to the nitrile ligands and the third being *trans* to the iron-bonded carbonyl group (Scheme 5, Figure 2). The

coupling between these two types of phosphorus nuclei is $^2J_{\text{PP}} \approx 70$ Hz in each case (Table 3). The C_s symmetry of the coordination polyhedron around the iron center is corroborated by the ^1H NMR spectroscopic data of compounds **3**; two types of methylene groups are observed for the tripodal framework in the $^1\text{H}\{^{31}\text{P}\}$ NMR spectra of compounds **3** (Table 3). While the signal with a relative intensity of *two* would be expected to be a singlet, the other one with the observed relative intensity of *four* might be expected to show a more complicated pattern due to the diastereotopicity of the relevant methylene protons. However, the differentiation between these two types of protons is evidently too small to be observable with the resolution of our experiment and only an apparent singlet signal is observed for these protons (Table 3). The ^{13}C NMR spectra of the trinuclear complexes **3** show signals due to the iron-bonded carbonyl group, the carbonyl groups bonded to the chromium (FeCr₂ compounds **3a** and **3b**) or manganese centers (FeMn₂ compound **3c**), and the bridging cyanide groups (Table 3).

The presence of the $(\eta^6\text{-CF}_3\text{C}_6\text{H}_5)$ moieties in **3b** is evident from their NMR signature. The ^1H NMR signals observed for this group in the spectrum of the potassium salt **K1b** are also observed in that of **3b**, with only very slight shift differences (Table 3). The ^{13}C NMR spectrum of **3b** shows signals due to the $\text{CF}_3\text{C}_6\text{H}_5$ ligands in the same spectral region as observed for **K1b**. In the ^{13}C NMR spectrum of **3b**, the CF_3 groups give rise to a quadruplet, which is partly obscured by the group of signals due to the *tripod* aryl carbon atoms. The arene carbon atoms of the $\text{CF}_3\text{C}_6\text{H}_5$ ligands, giving one signal each for the *ipso*, *ortho*, *meta*, and *para* carbon atoms in the spectrum of **K1b**, appear in part as pairs of signals in the spectrum of **3b** (Table 3). The reason for this side differentiation is not clear. It appears improbable that the two $\text{Cr}(\eta^6\text{-CF}_3\text{C}_6\text{H}_5)(\text{CO})_2$ units would be fixed in **3b** such as to have different time-averaged chemical environments. A loss of the C_s symmetry of the environment due to the chirality of the $\{\text{tripodFe}(\text{CO})\text{-NC-}(\eta^6\text{-CF}_3\text{C}_6\text{H}_5)\text{Cr}(\text{CO})_2\}$ residue would appear to offer a more probable explanation.

The presence of the π -bonded $\text{CH}_3\text{C}_5\text{H}_4$ group in the FeMn₂ compound **3c** is evident from its characteristic ^1H NMR signals (Table 3). The methyl substituent gives rise to a signal at $\delta = 2.0$, while the C_5H_4 fragment gives a partly

Table 3. NMR-spectroscopic data for compounds **PPN2** and **3**

	PPN2	3a	3b	3c
$^1\text{H}\{^{31}\text{P}\}$ NMR				
<i>tripod</i> -CH ₃	1.37 s, 3 H	1.64 s, 3 H	1.61 s, 3 H	1.61 s, 3 H
<i>tripod</i> -CH ₂	2.19 s, 6 H	2.35 s, 4 H	2.29 s, 4 H	2.30 s, 4 H
		2.75 s, 2 H	2.68 s, 2 H	2.67 s, 2 H
ligand ^[a]	—	—	4.7–5.2 m, 10 H	1.98 s, 3 H
				4.3–4.6 m, 8 H
CH _{arom}	7.1–7.7 m, 30 H	6.9–7.9 m, 30 H	7.0–7.9 m, 30 H	7.0–8.1 m, 30 H
$^{13}\text{C}\{^1\text{H}\}$ NMR				
<i>tripod</i> -CH ₃	38.0 q	37.7 q	37.8 q	38.0 m
<i>tripod</i> -CH ₂	33.9 m	30.9 m	30.6 m	31.0 m
		32.8 m	33.3 m	33.5 m
<i>tripod</i> -C _q	36.5 s	36.5 br	36.4 m	36.7 br
<i>tripod</i> -C _{arom}	132–135 m	128–134.5 m	128–134 m	128–135 m
<i>tripod</i> -C _{q,arom}	137–138 m	135.5–137.5 m	136–138 m	136–138 m
ligand-C ^[b]	—	—	126.0 q (CF ₃)	14.7 (CH ₃)
			($^1J_{\text{CF}} = 270$ Hz)	
ligand-C _{arom}	—	—	90.0 s (<i>p</i>)	82 br
			88.4 q (<i>i</i>)	
			($^2J_{\text{CF}} = 35$ Hz)	
			86.3 s/85.9 s (<i>m</i>)	
			85.2 m/84.1 m (<i>o</i>) ^[c]	
CN	172.1 s	182.8 s	195.4 s	191 br
ligand-CO	222.2 s	220.6 s	239.7 s	235 br
	218.0 s	217.3 s	239.8 s	
Fe-CO	—	213.5 dt	214.5 dt	216 m
		($^2J_{\text{CPcis}} = 20$ Hz)	($^2J_{\text{CPcis}} = 20$ Hz)	
		($^2J_{\text{CPtrans}} = 50$ Hz)	($^2J_{\text{CPtrans}} = 50$ Hz)	
$^{31}\text{P}\{^1\text{H}\}$ NMR				
<i>tripod</i> -PPh ₂	37.5 s	36.5 d, 2 P	36.1 d, 2 P	36.0 d, 2 P
		10.7 t, 1 P	9.0 t, 1 P	8.2 t, 1 P
		($^2J_{\text{PPcis}} = 68$ Hz)	($^2J_{\text{PPcis}} = 69$ Hz)	($^2J_{\text{PPcis}} = 68$ Hz)

[a] The ^1H NMR resonances of the ligands are found at $\delta = 4.5$ –5.1 (**K1b**, [D₆]acetone) and $\delta = 4.4$ (C₅H₄), 1.9 (CH₃) (**K1c**, [D₆]acetone)^[9b,12b]. — [b] The ^{13}C NMR resonances of the ligands are found at $\delta = 221.5$, 218.5 (CO) and 153.8 (CN) (**Na1a**, CD₃CN)^[12]; $\delta = 241.3$ (s, CO), 168.0 (s, CN), 126.4 (q, CF₃; $^1J_{\text{FC}} = 270$ Hz), 89.6 (s, C_{ar}), 86.5 (q, C_{ipso}; $^2J_{\text{FC}} = 35$ Hz), 86.3 (s, C_{ar}), 84.3 (s, C_{ar}) (**K1b**, [D₆]acetone). — [c] The signals are split due to $^3J_{\text{CF}}$ coupling.

resolved multiplet. In the spectrum of **K1c**, the expected A₂B₂ multiplet is unresolved,^[12b] as is often observed for compounds of this type. The form of this signal seen for **3c**, like that observed for **3b**, is suggestive of side differentiation induced by the prochirality of the compound. The structures of the trinuclear complexes **3** have been elucidated by X-ray crystallography (Tables 4 and 8). The basic molecular arrangement is the same in all three compounds, hence only the representative structure of **3b** is shown in Figure 2. The coordination around the iron center is idealized octahedral with the *tripod* ligand occupying one face of the octahedron. The organometallic ligands are consequently in a mutually *cis* arrangement with the coordination octahedron being completed by the iron-bonded carbonyl ligand (Figure 2).

All three organometallic ligands have at least two mutually *cis*-carbonyl groups that are also *cis* to the cyano bridging group. These carbonyl groups show roughly the same orientation with respect to the *tripod*iron(II) entity in all three cases (Table 4). The torsion angles χ defined by the rotational position of the carbonyl groups around an Fe–M axis [M = Cr (**3a** and **3b**), Mn (**3c**)] with respect to the idealized trigonal axis of the *tripod*iron entity are very

similar for these four groups in the three compounds **3**. This means that three of the carbonyl groups of the pentacarbonylmetal entities in **3a** are formally replaced by η^6 -arene units (FeCr₂ compound **3b**) or η^5 -cyclopentadienyl units (FeMn₂ compound **3c**) without a significant change in the position of the two remaining carbonyl groups. These carbonyl groups, like those in **2**[–], show short contacts to some of the phenyl protons of the *tripod* entity (Table 4). Geometrically, these contacts are again rather similar for all three compounds. Thus, the rotational positions of the aryl groups (Figure 2) of the *tripod*iron entity are also rather similar for all three species (Table 4). Overall, in fact, the crystals of **3a**, **3b** (FeCr₂), and **3c** (FeMn₂) are isotypic (Table 8). The Fe–P bond lengths are in the normal range, with the bonds to the phosphorus atom *trans* to the carbonyl groups being longer than the other two Fe–P bonds (Table 4). The Fe–N bond lengths are in the range 195.7(3)–198.5(4) pm (Table 4) and are distinctly longer than the Fe–C_{CO} bonds [179.5(5)–180.5(2) pm] in each case. The Fe–N–C entities deviate from linearity, as is generally observed for *tripod*iron(II) nitrile compounds.^[1,2,13] The deviation is smaller in **3a** than in **3b** or **3c** (Table 4), reflecting the lower symmetry of the organometallic termini

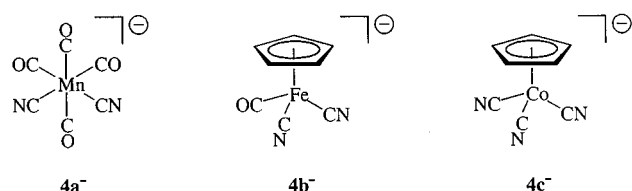
Table 4. Bond lengths and angles in the trinuclear complexes **3**

	3a	3b	3c
Fe–P _{cisCO}	228.9(1)/226.2(1) ^[a]	227.0(1)/225.8(1)	226.6(1)/224.8(1)
Fe–P _{transCO}	230.2(1)	230.3(1)	229.9(1)
Fe–N	196.3(3)/195.8(3)	198.2(2)/195.9(2)	198.5(4)/195.7(4)
Fe–C	180.1(4)	180.5(2)	179.5(5)
M–C _{CN} ^[b]	204.2(3)/203.7(4)	199.9(2)/199.0(2)	191.5(5)/190.0(5)
C–N	115.2(4)/115.3(4)	116.1(3)	115.5(6)/116.4(6)
M–C _{CO}	185.8(3)/185.7(4) (<i>ax</i>)	—	—
	188.8(4)–192.2(4) (<i>eq</i>)	183.7(3)–184.7(3)	173.4(4)–176.6(4)
M–MP ^[c]	—	166.8/167.2	177.3/177.3
Fe–N–C	169.9(3)/169.1(3)	164.2(2)/157.1(2)	165.1(4)/158.5(4)
M–C–N	179.0(3)/176.4(3)	177.8(2)/175.2(2)	177.9(4)/177.5(4)
P–Fe–P	86.83(4)–90.77(4)	87.00(3)–91.28(3)	86.74(4)–90.88(4)
N–Fe–N	84.2(1)	84.1(1)	84.5(1)
O...H ^[d]	271/288	262/284	276/297
F...H ^[e]	—	265/292	—
τ ₁ ^[f]	26.8(3)	26.7(2)	26.4(3)
τ ₂	16.2(3)	19.0(2)	16.8(4)
τ ₃	29.7(3)	33.4(2)	30.9(3)
φ ₁ ^[g]	–61.6	–62.4	–58.7
φ ₂	–37.9	–27.9	–27.9
φ ₃	+22.6	+24.1	+25.6
φ ₄	+36.6	+39.0	+38.7
φ ₅	+21.9	+15.4	+18.4
φ ₆	–5.3	–9.4	–6.6
χ _a ^[h]	–156	–146	–154
χ _b	–69	–65	–63
χ _c	–72	–80	–80
χ _d	+18	+10	+16

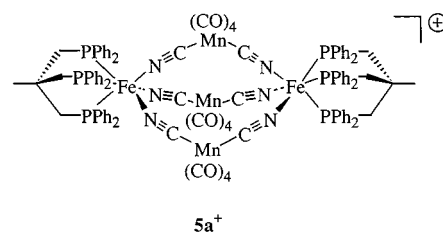
^[a] The values in parentheses are standard deviations in units of the last decimal listed. – ^[b] M = Cr (**3a**, **3b**), Mn (**3c**). – ^[c] MP is the center of the π -coordinated cyclic ligand in the organometallic units of complexes **3b** and **3c**. – ^[d] Shortest distances between a carbonyl oxygen atom of each of the two carbonylmetal moieties and a hydrogen atom of a *tripod* phenyl substituent. – ^[e] Shortest distances between a fluorine atom and a hydrogen atom of a *tripod* phenyl substituent. – ^[f] τ denotes the torsion angles Fe–P–C–C within the chelate cages. – ^[g] ϕ designates the torsion angles C_{ortho}–C_{ipso}–P–Hz, where Hz is the endpoint of a vector vertical to the plane spanned by the three phosphorus nuclei and fixed to one phosphorus center, pointing in the direction of the observer with respect to Figure 2, **A**. – ^[h] χ = Hx–Fe–M–O_{CO} denotes the torsion angle Hx–Fe–M–O_{CO,eq}, where Hx is the endpoint of a vector radiating from the iron center along the idealized C₃ axis in a direction away from the observer with respect to Figure 2, **A**.

in the latter compounds. The geometries of the organometallic termini themselves are unremarkable (Table 4).

While compounds **2**[–] (FeCr₃) and **3** (FeCr₂, FeMn₂) contain organometallic groups linked by a *tripod*-iron–diisocyano group (Scheme 1, **B**), the reaction of *tripod*-iron(II) entities with organometallic dinitriles should lead to compounds containing two *tripod*-iron(II) entities linked by a metal–dinitrile species (Scheme 1, **A**). Quite a number of anionic organometallic dinitriles are known and some of them have been shown to be suitable building blocks for the construction of oligometallic cage compounds.^[3b,3c,14] The dicyanometalates **4**[–] (Scheme 6) are obtained by standard procedures.^[15]

Scheme 6. Dicyanometalate ligands **4**[–]

When an equimolar solution of *tripod* and FeCl₂ in acetone is treated with an equimolar amount of **K4a**, the initially faintly yellow solution immediately turns red. Whereas we had hoped to obtain a tetrametal square with two *tripod*FeL entities and two Mn(CO)₄ constituents at its corners by applying this stoichiometry, compound **5a**⁺ (Scheme 7) was obtained as the only characterizable product in very low yield (see Exp. Sect.).

Scheme 7. The constitution of the pentanuclear cation **5a**⁺

5a⁺ was identified by X-ray crystallography of its FeCl₄[–] salt, which was serendipitously found to crystallize. **5a**⁺ is a pentanuclear Fe₂Mn₃ compound^[16] composed of two *tripod*-iron(II) entities, which are bridged by the *cis*-dicyano-

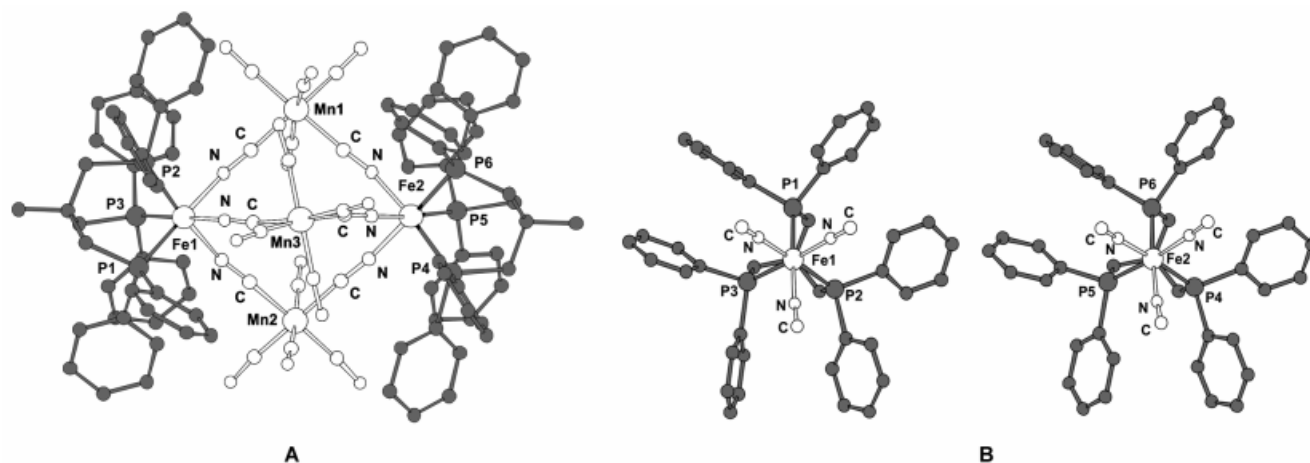


Figure 3. Structure determination of **5aFeCl₄**: A: view of the pentanuclear cation **5a⁺**; B: standardized view of the two *tripod*iron(II) centers

manganese parts of three (tetracarbonyl)dicyanomanganate bridging units (Figure 3).

5a⁺ has approximate *C*₂ symmetry (*C*₂ axis along the bisector of Fe1–Mn3–Fe2 in Figure 3, A). This symmetry is not imposed by crystal symmetry, but is evident from inspection of Figure 3, A, as well as from the values of the geometric parameters, pairs of which should be equal under this symmetry (Table 5).

Table 5. Bond lengths and angles in the pentanuclear cation **5a⁺**

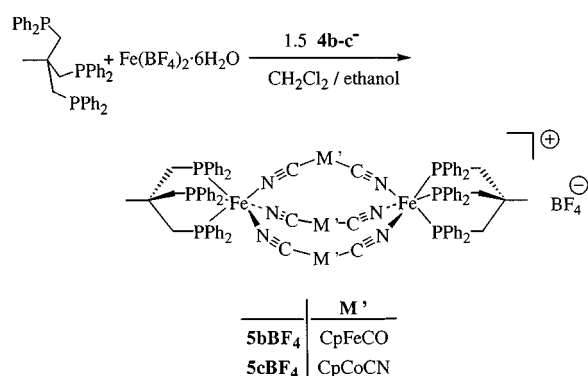
Fe–P	226.1(2)–228.4(2) ^[a]	Fe...Mn	507–511
Fe–N	195.1(7)–197.5(7)	τ ₁ ^[b]	40.4(6)/43.0(6)
Mn–C _{CN}	198(1)–201(1)	τ ₂	27.7(7)/31.7(7)
Mn–C _{CO,cis}	186(1)–188(1)	τ ₃	26.3(6)/28.2(6)
Mn–C _{CO,trans}	182(1)–185(1)	φ _I ^[c]	+1.5/–2.0
Fe–N–C	168.6(6)–173.2(7)	φ _{II}	–25.8/–30.0
Mn–C–N	172.2(7)–177.3(7)	φ _{III}	–61.6/–53.7
P–Fe–P	85.8(1)–91.4(1)	φ _{IV}	–43.2/–42.8
N–Fe–N	83.8(3)–85.5(3)	φ _V	+9.6/–34.5
C–N	114(1)–116(1)	φ _{VI}	–16.3/–28.0

^[a] The values in parentheses are standard deviations in units of the last decimal listed. – ^[b] The τ values refer to the torsion angles Fe–P–C–C within the chelate cages; they are arranged in pairs to reflect the approximate *C*₂ symmetry of the cation **5a⁺**. – ^[c] φ describes the torsion of the phenyl rings of the *tripod*iron entities. The torsion relates to the rotation around the corresponding P–C_{ipso} axis with the idealized trigonal axis of the *tripod*iron fragment as the reference axis. The first value φ_I describes the rotation of the phenyl group at P1, which points towards the observer in Figure 3, A, with the companion phenyl group at P6 again pointing towards the observer. Starting from this phenyl group at P1, the six pairs of values φ_I–φ_{VI} are listed in a counterclockwise sequence, when looking at Fe1 from the location of Fe2 (Figure 3, A and B).

Thus, even the torsion angles φ describing the orientation of the phenyl groups at the two *tripod*iron entities, as well as the twist angles τ describing the skew of the chelate cage, are in good pairwise agreement (Figure 3, B; Table 5). The Fe–N–C angles deviate from linearity in a systematic way. If, as initially expected, only two sites at each *tripod*iron entity were to be coordinated by the cyano groups of two

(tetracarbonyl)dicyanomanganate units, a strain-free square arrangement with linear Fe–N–C groups would result, with the vacant coordination site at each *tripod*iron entity being perpendicular to the plane of this square. These coordination sites have to be brought into an arrangement that allows them to be spanned by the additional Mn(CN)₂ unit. This induces some strain in the scaffolding, which results in a bending of the Fe–N–C angles. As is well known, these angles are rather tolerant to this type of deformation (Figure 3; Table 5).

In view of the fact that pentanuclear compounds such as the Fe₂Mn₃ complex **5a⁺** are formed even under stoichiometric conditions, which should favor the formation of square tetranuclear aggregates, the stoichiometry was changed to *tripod*/Fe^{II}/M'(CN)₂[–] = 2:2:3. According to this protocol, the pentanuclear compounds **5bBF₄** (Fe₅) and **5cBF₄** (Fe₂Co₃) were prepared (Scheme 8).

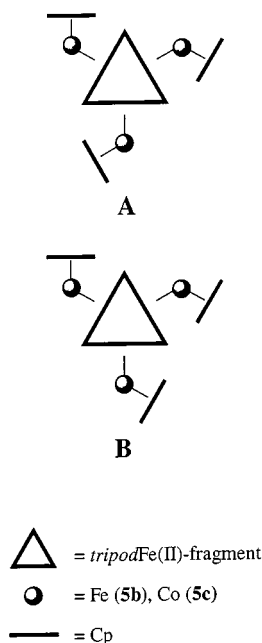


Scheme 8. Synthesis of **5bBF₄** and **5cBF₄**

Upon work-up of the respective reaction mixtures, microcrystalline red powders were obtained, which were shown by NMR spectroscopy to contain different diastereomers. With **5b⁺** (Fe₅), the reaction product showed four signals in the cyclopentadienyl region of the ¹H NMR spectrum. By repeated recrystallization, a product was obtained that showed one of these Cp peaks with 95% of the total intens-

ity. The cyclopentadienyl resonance of the crude product is clearly composed of two sets of signals, one being a sharp singlet at $\delta = 4.1$ and the other one being composed of three signals of equal intensity (see Exp. Sect.).

The intensity ratio of these two sets of signals is initially 2:1, whereas it becomes 19:1 following the recrystallization process. These observations may be explained as follows: There are two possible basic arrangements for the mutual orientation of the Cp groups in a compound of type **5b**⁺ (Fe₅). One of them conforms to the constitutional C₃ symmetry (Scheme 9, A), while in the other this symmetry is lost (Scheme 9, B). There are six different possibilities for creating this unsymmetrical type of arrangement (Scheme 9, B), whereas there are only two possibilities for generating a C₃-symmetric arrangement (Scheme 9, A). The statistical probability of formation of the C₃-symmetric species is hence 0.25. The C₃-symmetric species will give rise to just one single Cp resonance, while for the unsymmetrical species three Cp signals of equal intensity can be expected. This is indeed what is observed in the ¹H NMR spectrum of crude **5b**⁺. The ratio of the symmetrical to the unsymmetrical diastereomers is initially 2:1, which is quite different from the ratio expected on statistical grounds. This suggests that the C₃-symmetric product is formed under considerable diastereoselective control. Crystallization enriches the sample in the symmetrical product (Scheme 9, A), which is present to an extent of 95% after three recrystallizations.



Scheme 9. Diastereomers of **5b**⁺ and **5c**⁺

Diastereoselectivity is also observed in the formation of **5c**⁺ (Fe₂Co₃). In this case, the C₃-symmetric isomer is isolated as the sole product in 40% yield after just one recrystallization step. **5cBF**₄ (Scheme 9, A) shows only one sharp Cp signal at $\delta = 4.7$ in its ¹H{³¹P} NMR spectrum. The protons of the methylene groups of the tripod ligands are

diastereotopic and give rise to a doublet-of-doublets signal in the ¹H{³¹P} NMR spectrum (see Exp. Sect.). Likewise, the phenyl groups of the PPh₂ donors of the tripod ligands are diastereotopic. The ¹³C NMR signals fall into two well-separated groups, consisting of a multiplet due to the *ortho*, *meta*, and *para* carbon atoms and a well-resolved signal due to the *ipso* carbon atoms (see Exp. Sect.). The pentanuclear structure of **5**⁺ was unequivocally established from these findings, as were the structures of **5a**⁺ (Fe₂Mn₃), **5b**⁺ (Fe₅), and **5c**⁺ (Fe₂Co₃) by the aforementioned combination of analytical methods.

The FAB⁺ mass spectra show peaks due to the molecular ion **5**⁺ in each case, accompanied by peaks originating from [**5** – tripod]⁺ (Table 6). The infrared spectrum of **5a**⁺ (Table 6) shows the presence of the organometallic (CO)₄Mn(CN)₂ building blocks through the characteristic patterns of its ν_{CO} and ν_{CN} bands, which are similar to those seen for **K4a**. Although the ν_{CO} absorptions are seen at wavelengths similar to those found for **K4a**, they show a somewhat more complicated structure than in the case of this starting material (Table 6). This observation may be similarly explained as previously proposed for the pair of compounds **Na1a** and **PPN2** (FeCr₃). **5bBF**₄ shows ν_{CN} bands at 2140 cm^{−1} and 2106 cm^{−1}, positions not dissimilar from those of the bands reported for **K4b**.^[17] The ν_{CO} band of **5bBF**₄ is observed at 1961 cm^{−1}, and is thus shifted to higher energies relative to the ν_{CO} absorption of **K4b**. The (cyclopentadienyl)tricyanocobalt(III) units of **5cBF**₄ (Fe₂Co₃) give rise to a band at 2168 cm^{−1}, which is broader and more intense than a second band at 2126 cm^{−1}. This latter band is attributed to the ν_{CN} vibrations of the terminally bonded cyano ligands, while the former is interpreted as being the envelope of the two ν_{CN} vibrations of the bridging cyano groups.

Electrochemistry and UV/Vis Spectroscopy

All compounds **PPN2**, **3**, and **5BF**₄ contain the tripodiron(II) entity coordinated to at least two nitrile functions. A band at $\lambda \approx 20000$ cm^{−1} appears to be characteristic of iron(II) compounds of this type (Table 7). Irrespective of whether the nitrile functions originate from bridging cyano groups or from organic nitriles, this is a constant signature for all [tripodFe^{II}(NCR)₃]ⁿ⁺ species and obviously for all [tripodFe^{II}(NCR)₂L]ⁿ⁺ species as well. The energy of this transition is fairly constant for all compounds of this type.^[2,13] A band at shorter wavelengths at $\lambda \approx 25000$ cm^{−1} is somewhat more variable with respect to its energy and extinction coefficient (Table 7), but also appears to be characteristic of compounds containing a tripodFe^{II}(NCR)₃ or a tripodFe^{II}(NCR)₂L (**3a**) moiety.^[2,13] Based on the intensities of the relevant bands, the underlying electronic transitions must involve some charge-transfer character. At the short wavelength side, a band is present at $\lambda \approx 30000$ cm^{−1}, although it is not always observable as it may be obscured by the steep rise of shorter wavelength bands. A band in this position has also been observed for other tripod-Fe^{II}(NCR)₂L compounds.^[2,13]

Table 6. Spectroscopic and analytical data of compounds **5aFeCl₄**, **5bBF₄**, and **5cBF₄**

No.	Formula (M [g/mol])	MS <i>m/z</i>	[Frag.]	C _{calcd.} , H _{calcd.} , N _{calcd.} C _{found.} , H _{found.} , N _{found.}	IR (CsI): $\tilde{\nu}$ [cm ⁻¹] ^[a] ν_{CN} ν_{CO}
5aFeCl₄	C ₁₀₀ H ₇₈ Cl ₄ Fe ₃ Mn ₃ N ₆ O ₁₂ P ₆ (2215.8)	2018 1680	[M] ⁺ [M – 12 CO] ⁺	54.21, 3.55, 3.79 53.30, 4.45, 3.59	2155 w 2091 m 2005 vs, 1987 vs
5bBF₄	C ₁₀₆ H ₉₃ BF ₄ Fe ₅ N ₆ O ₃ P ₆ (2050.8)	1963 1339	[M] ⁺ [M – <i>tripod</i>] ⁺	62.07, 4.57, 4.10 61.72, 4.65, 4.25	2140 s 2106 m 1961 vs
5cBF₄	C ₁₀₆ H ₉₃ BCO ₃ F ₄ Fe ₂ N ₉ P ₆ (2054.1)	1966 1342	[M] ⁺ [M – <i>tripod</i>] ⁺	61.97, 4.56, 6.14 60.55, 4.76, 6.07	2168 s – 2126 m –

^[a] IR absorptions of the potassium salts of the organometallic ligands [cm⁻¹]: 2145 w, 2103 vw, 2030 vs, 1952 vs^[15a] (**K4a**); 2094, 2088, 1949^[17] (**K4b**); 2130 s, 2124 vs, 2120 vs^[15c] (**K4c**).

Table 7. Cyclovoltammetric and UV/Vis-spectroscopic data of compounds **PPN2**, **3**, and **5BF₄**; reference data for dinuclear compounds with dicyanamido- (**A**⁺) and dicyanmethanido-bridged (**B**⁺) dinuclear *tripod*iron(II) complexes (Scheme 11)^[2c]

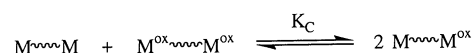
No.	CV <i>E</i> _{1/2} [mV]	<i>E</i> _{1/2} [mV]	$\Delta E_{1/2}$ [mV]	<i>K_C</i> ^[a]	$\delta\Delta G_{298}$ ^[b] [kJ/mol]	UV λ [cm ⁻¹] (ϵ [M ⁻¹ cm ⁻¹])	Bridging unit
2 ⁻	425 ^[c]	780	355	1·10 ⁶ ^[d]	34	30200 (11000)	–CN–Fe ^{II} –NC–
2	780 ^[f]	900	120	1·10 ²	12	–	–CN–Fe ^{II} –NC–
3a	825 ^[f]	993	168	6·10 ²	16	30000 (6000)	–CN–Fe ^{II} –NC–
3b	88 ^[f]	252	164	6·10 ²	16	–	–CN–Fe ^{II} –NC–
5b ⁺	652 ^[g]	865 ^[g]	213	4·10 ³	21	31900 (5000)	–NC–Fe ^{II} –CN–
5c ⁺	939 ^[g]	1084 ^[g]	145	3·10 ²	14	26000 (5000)	–NC–Co ^{III} –CN–
A ⁺	910 ^[g]	1150 ^[g]	240	1·10 ⁴	23	24200 (900)	–NC–N ⁻ –CN–
B ⁺	1120 ^[g]	1400 ^[g]	280	5·10 ⁴	27	24300 (1100)	–NC–C(R) ⁻ –CN–

^[a] Equilibrium constants *K_C* for the comproportionation reaction (Scheme 10) calculated from $K_C = \exp\{\Delta E_{1/2}/25.69\}$; $\Delta E_{1/2}$ in mV. – ^[b] $\delta\Delta G_{298}$ calculated from the differences $\Delta E_{1/2}$ between the oxidation potentials of the first and second oxidation steps. – ^[c] The negative charge of **2**⁻ leads to a value for the first oxidation potential about 400 mV lower than that observed for **3a**. – ^[d] The extent of electronic coupling is greatest for the negatively charged complex **2**⁻. – ^[e] Band is obscured by the steep rise of shorter wavelength bands. – ^[f] The Cr(CO)₅CN groups of **2**⁻ and **3a** are less easily oxidized than the Cr(CF₃C₆H₅)(CO)₂CN group of **3b**: $E_{\text{pa}}\{\text{K}[\text{Cr}(\eta^6\text{-CF}_3\text{C}_6\text{H}_5)(\text{CO})_2\text{CN}], \text{K1b}\} = -100$ mV (vs. SCE, CH₃CN), $E_{1/2}\{\text{Na}[\text{Cr}(\text{CO})_5\text{CN}], \text{Na1a}\} = +690$ mV (vs. SCE; reversible, CH₃CN).^[12] – ^[g] The oxidation potentials of the dinuclear compounds increase with the estimated electronegativity of the central atom (right column) in the bridging moieties.

Cyclic voltammetry shows a minimum of two reversible one-electron oxidation steps for compounds **PPN2**, **3**, and **5BF₄**. Compounds **PPN2** (FeCr₃) and **3** (FeCr₂) contain a *tripod*Fe^{II}L entity at the bridging position between two organometallic cyano compounds. [*tripod*Fe^{II}(NCMe)₃]²⁺ ^[13] is only oxidized at 1400 mV (CH₃CN; reversible vs. SCE), while the organometallic nitriles bonded to this bridging group in **3** are more easily oxidized [$E_{1/2}\{\text{Na}[(\text{CO})_5\text{CrCN}]; \text{Na1a}\} = +690$ mV (CH₃CN; reversible vs. SCE);^[12] $E_{\text{pa}}\{\text{K}[(\eta^6\text{-CF}_3\text{C}_6\text{H}_5)\text{Cr}(\text{CO})_2\text{CN}]; \text{K1b}\} = -100$ mV (CH₃CN; vs. SCE; see Exp. Sect.)]. The oxidation waves observed for **3a** and **3b** (Table 7) are thus in the characteristic range for the one-electron oxidations of the terminal groups. Compared to the corresponding alkali metal salts, the oxidation potentials of the iron-coordinated organometallic nitriles are shifted to higher potentials by around 200 mV (Table 7), as would be expected for the oxidation of a

neutral compound compared with the oxidation of an anion. The appearance of two well-separated one-electron oxidation steps for **3a** and **3b** implies electronic conjugation between the two organometallic termini. Purely electrostatic coupling cannot account for the difference in $\Delta E_{1/2}$ of around 165 mV observed between these two cases^[18] (Table 7) for two centers about 600 pm apart as they are in **3**.

The comproportionation constant (Scheme 10) for the reaction is 6×10^2 for both FeCr₂ compounds **3a** and **3b** (Table 7). It is thus in a range characteristic of class III mixed-valence compounds^[19] and may be taken as proof of



Scheme 10. Comproportionation equilibrium

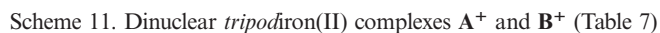
amples of 2^- , 3 , and 5^+ , the mixed-valence species are definitely of type III.^[19]

A comparison can now be made between the conjugation capacities of dicyanometalate bridges and main-group-based anionic dicyano bridges. Several compounds containing two *tripod*iron(II) entities coupled by dicyanamido or dicyanomethanido ligands are known^[2] (Scheme 11; **A**⁺, **B**⁺). Their electrochemical properties are very similar to those observed for **5b**⁺ and **5c**⁺ (Table 7). The relevant comproportionation constants resulting from conjugation through the organic linkers are $K_C \approx 10^4$ and are thus not significantly different from the values observed with either organometallic dicyanometalate or *tripod*Fe^{II}(CN)₂ linking groups. It appears that the HOMO of such compounds does not have a large orbital coefficient at the central atom of the bridging group, be it a main-group element or a transition metal. In each case studied, this central group is far more difficult to oxidize than the termini.

With monocyano-metalates $[M-CN]^-$ (1^-), the *tripodiron*(II) template selectively forms tetranuclear species $[tripodFe\{NC-M\}_3]^-$ (2^-) or trinuclear entities $[tripodFe(CO)\{NC-M\}_2]$ (**3**) under the appropriate stoichiometric control. Dicyano-metalates $[M'(CN)_2]^-$ (4^-) form pentanuclear compounds $[tripodFe\{NC-M'-CN\}_3-Fe-tripod]^+$ (5^+). The organometallic termini M in compounds 2^- and **3** [e.g. $Cr(CO)_5$] are more easily oxidizable than the *tripodiron*(II) entity. Cyclic voltammetry reveals stepwise one-electron oxidation of these termini with potential differences characteristic of conjugative coupling between them. In compounds 5^+ , with M' being $CpFe(CO)$ (**5b** $^+$) or $CpCo(CN)$ (**5c** $^+$), the *tripodiron*(II) entities are more easily oxidized than the organometallic bridging units. Cyclic voltammetry shows two well-separated, reversible, one-electron oxidation steps, which is consistent with strong conjugative coupling of the iron centers through the organometallic $M'(CN)_2$ linkers. It has been observed that the coupling efficiency of $M'(CN)_2^-$ is similar to that of $[RC(CN)_2]^-$ in structurally analogous compounds.

Experimental Section

General Remarks: All manipulations were carried out under argon by means of standard Schlenk techniques. All solvents were dried by standard methods^[20] and distilled under argon. Silica gel and kieselguhr used for filtrations and chromatography were degassed at 1 mbar for 24 h and saturated with argon. The compounds **Na1a**,^[9] **K1c**,^[9] *tripod*,^[21] **K4a**,^[15a] **K4b**,^[15b] **K4c**,^[15c] and $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ ^[22] were prepared according to or by adaptation of literature procedures. All other chemicals were obtained from commercial suppliers and were used without further purification. – NMR: Bruker Avance DPX200 spectrometer operating at 200.13 MHz (¹H), 50.323 MHz (¹³C), 81.014 MHz (³¹P); *T* = 303 K; chemical shifts (δ) in ppm with respect to CD_2Cl_2 (¹H: δ = 5.32; ¹³C: δ = 53.5), $[\text{D}_6]\text{acetone}$ (¹H: δ = 2.05; ¹³C: δ = 20.8,



206.1), or $[\text{D}_6]\text{DMSO}$ (^1H : $\delta = 2.50$; ^{13}C : $\delta = 39.4$) as internal standards; ^{31}P chemical shifts (δ) in ppm with respect to 85% H_3PO_4 (^{31}P : $\delta = 0$) as an external standard; CD_2Cl_2 , $[\text{D}_6]\text{acetone}$, and $[\text{D}_6]\text{DMSO}$ used for NMR-spectroscopic measurements were degassed by three successive freeze-pump-thaw cycles and dried with 4 Å molecular sieves. – IR: Biorad Excalibur FTS 3000 spectrophotometer (samples in CsI discs or as solutions between CaF_2 windows). – UV/Vis spectra: Perkin–Elmer Lambda 9 UV/Vis spectrophotometer; ca. 10^{-3} M solutions in CH_2Cl_2 . – MS: Finnigan MAT 8320 operated in FAB mode (xenon; matrix: 4-nitrobenzyl alcohol). – Cyclic voltammetry: EG&G Princeton Applied Research model 273 potentiostat; potentials in mV versus SCE at a glassy carbon electrode at 25 °C; sample solutions: ca. 10^{-3} M in 0.1 M Bu_4NPF_6 in CH_3CN or CH_2Cl_2 . – Elemental analyses: Microanalytical Laboratory of the Organisch-Chemisches Institut, Universität Heidelberg.

Potassium [Dicarbonyl(cyano)(η^6 -trifluoromethylbenzene)chromate(0)] (K1b): Tricarbonyl(η^6 -trifluoromethylbenzene)chromium (1.72 g, 6.1 mmol) and potassium cyanide (1.14 g, 17.5 mmol) were dissolved in methanol (200 mL) in an irradiation vessel. The vessel was cooled to 0 °C and the solution was irradiated for 3 h with UV light from a high-pressure mercury lamp (Hanau TQ 150). After allowing the dark-brown reaction mixture to warm to room temperature, it was filtered and the filtrate was concentrated to dryness. The residue was washed with diethyl ether (100 mL) and filtered through 5 cm of kieselguhr with tetrahydrofuran (100 mL). Evaporation of the solvent from the orange-red filtrate and subsequent crystallization of the residue from acetone/petroleum ether (boiling range 40–60 °C) yielded **K1b** as a microcrystalline solid with an intense orange color (900 mg, 46%). – $\text{C}_{10}\text{H}_5\text{CrF}_3\text{KNO}_2$ (319.2): calcd. C 37.62, H 1.58, N 4.39; found C 36.93, H 1.89, N 4.48. – ^1H NMR ($[\text{D}_6]\text{acetone}$): $\delta = 4.5\text{--}5.1$ (m). – ^{13}C NMR ($[\text{D}_6]\text{acetone}$): $\delta = 241.3$ (s, CO), 168.0 (s, CN), 126.4 (q, CF_3 , $^1J_{\text{FC}} = 270$ Hz), 89.6 (s, C_{ar}), 86.5 (q, $\text{C}_{\text{ar}}\text{CF}_3$, $^2J_{\text{FC}} = 35$ Hz), 86.3 (s, C_{ar}), 84.3 (s, C_{ar}). – IR (CH_3OH): $\tilde{\nu} = 2041$ w, br (CN), 1910 s, 1856 s (CO). – MS (FAB $^-$): $m/z = 280.0$ $[\text{M}]^-$. – CV (CH_3CN , SCE): $E_{\text{pa}} = -100$ mV (irrev. ox.).

PPN[*tripod*Fe{NC–Cr(CO) $_5$ }] $_3$ (PPN2): To a solution of FeCl_2 (0.29 mmol, 34 mg) and *tripod* (0.29 mmol, 184 mg) in acetone, a solution of **Na1a** (216 mg, 0.90 mmol) in acetone was added dropwise by means of a syringe. An immediate color change from pale-yellow to red was observed. After the addition of bis(triphenylphosphanyl)iminium chloride (PPNCl; 176 mg, 0.31 mmol), the reaction mixture was concentrated to dryness in vacuo. The red residue was redissolved in dichloromethane (20 mL) and the resulting red solution was stirred for 2 h at room temperature to complete the cation exchange. Filtration through 3 cm of kieselguhr gave a red solution, which was concentrated to a volume of 5 mL and layered with ethanol (20 mL). **PPN2**·0.75 CH_2Cl_2 was obtained as red needle-shaped crystals (280 mg, 52%). For analytical and spectroscopic data of **PPN2**, see Tables 2 and 3.

[*tripod*Fe(CO){NC–M}] $_2$ (3); M = Cr(CO) $_5$ (3a**), Cr(η^6 - $\text{CF}_3\text{C}_6\text{H}_5$)(CO) $_2$ (**3b**), Mn(η^5 - $\text{CH}_3\text{C}_5\text{H}_4$)(CO) $_2$ (**3c**):** To a solution of FeCl_2 (0.65 mmol, 34 mg) and *tripod* (0.65 mmol, 184 mg) in acetone, a solution of the alkali metal salt **Na1a** (**3a**), **K1b** (**3b**), or **K1c** (**3c**) (1.30 mmol) in acetone was added dropwise by means of a syringe. An immediate color change from pale-yellow to orange-red was observed. After bubbling carbon monoxide through the reaction mixture for 5 min, the turbid brown solution was concentrated to dryness in vacuo leaving a brown-red solid residue. This was redissolved in dichloromethane and the resulting solution was filtered through 3 cm of kieselguhr. The products were isolated in

the form of brown microcrystalline powders by addition of petroleum ether (boiling range 40–60 °C) to the concentrated brown-red filtrates. Crystals of **3a**, **3b**, and **3c** suitable for X-ray analyses were grown by layering dilute solutions in acetone with petroleum ether (boiling range 40–60 °C) at room temperature. For analytical and spectroscopic data of compounds **3a**, **3b**, and **3c**, see Tables 2 and 3.

[(*tripod*Fe) $_2$ {NC–M'–CN} $_3$]BF $_4$ (5BF $_4$**); M' = Fe(η^5 - C_5H_5)(CO) (**5bBF $_4$**), Co(η^5 - C_5H_5)(CN) (**5cBF $_4$**):** To a solution of $\text{Fe}^{\text{II}}\text{aq}(\text{BF}_4)_2$ (1.0 mmol, 338 mg) and *tripod* (1.0 mmol, 625 mg) in dichloromethane/ethanol (1:1, 40 mL), the potassium salt of the appropriate ligand, **K4b** (**5bBF $_4$**) or **K4c** (**5cBF $_4$**) (1.5 mmol), was added as a solid in a single portion. A color change from pale-yellow to red was observed. After stirring for 1 h at room temperature, the reaction mixture was concentrated in vacuo. The red residue was filtered through 1 cm of kieselguhr with dichloromethane. Evaporation of the solvent from the red filtrate and subsequent washing of the residue with diethyl ether left a red microcrystalline solid. The C_3 -symmetric isomers (Scheme 9, **A**) of the pentanuclear complexes were purified by recrystallization from dichloromethane/ethanol. Yields: **5bBF $_4$** : 42% (crude product), ca. 10% (symmetric isomer of **5bBF $_4$** , three recrystallizations); **5cBF $_4$** : 67% (crude product), 40% (symmetric isomer of **5cBF $_4$** , one recrystallization).

5bBF $_4$: $^1\text{H}\{^{31}\text{P}\}$ NMR (CD_2Cl_2): $\delta = 1.53$ (s, CH_3), 2.00–2.35 (m, CH_2), 4.10 (s, C_5H_5), 6.9–7.8 (m, H_{ar}). – ^{31}P NMR (CD_2Cl_2): $\delta = 37.4$ (s). – The unsymmetrical isomer of **5bBF $_4$** was not isolated in pure form. Its Cp resonances were seen as singlets at $\delta = 4.14$, 4.04, and 3.86 in the $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of the crude product.

5cBF $_4$: $^1\text{H}\{^{31}\text{P}\}$ NMR (CD_2Cl_2): $\delta = 1.43$ (s, CH_3), 2.0–2.4 (m, CH_2), 4.7 (s, C_5H_5), 7.0–7.8 (m, H_{ar}). – ^{31}P NMR (CD_2Cl_2): $\delta = 39.1$ (s). – ^{13}C NMR ($[\text{D}_6]\text{DMSO}$): $\delta = 138.6$ (dd, PC_{ar}), 136.9 (dd, PC_{ar}), 134.5–128.0 (m, C_{ar}), 133.7 (s, Co–CN–Fe), 117.9 (s, Co–CN), 88.9 (s, C_5H_5), 37.6 (m, CH_3), 36.4 (m, C_{q}), 32.8 (m, CH_3). – For further analytical and spectroscopic data of compounds **5bBF $_4$** and **5cBF $_4$** , see Tables 6 and 7.

Crystals of compound **5aFeCl $_4$** suitable for an X-ray crystallographic structure determination were obtained in very low yield (15 mg) from the reaction of FeCl_2 (135 mg, 1.07 mmol), *tripod* (680 mg, 1.09 mmol), and potassium tetracarbonyl(dicyano)manganate(I) (280 mg, 1.08 mmol) in acetone. After concentrating the reaction solution to dryness and filtration of the residue through 1 cm of kieselguhr with dichloromethane, the red filtrate was concentrated to dryness. Red parallelepiped-shaped crystals of **5aFeCl $_4$** were grown by vapor diffusion of diethyl ether into a solution of the crude product in tetrahydrofuran/ethanol at room temperature. – $^1\text{H}\{^{31}\text{P}\}$ NMR (CD_2Cl_2): $\delta = 1.5$ (br. s, CH_3), 2.3 (br. m, CH_2), 7.0–7.8 (m, H_{arom}); all signals are broad because of the paramagnetism of the FeCl_4^- anion. – ^{31}P NMR (CD_2Cl_2): $\delta = 32.7$ (s). – For further analytical and spectroscopic data, see Tables 5, 6, and 7.

Salts of **5a $^+$** with counteranions other than tetrachloroferrate(III) could not be obtained in analytically pure form, neither by the procedure described above for **5bBF $_4$** and **5cBF $_4$** nor under strictly anhydrous conditions. This is mainly due to problems associated with the purification of these compounds, which could not be effected by means of crystallization and chromatography.

X-ray Crystallographic Studies: Suitable crystals were taken directly from the mother liquor, immersed in perfluorinated polyether oil, and fixed to a glass capillary. Data were collected with a Nonius–Kappa CCD diffractometer (low-temperature unit, graph-

Table 8. Crystallographic data for compounds **PPN2**, **3**, and **5aFeCl₄**

Compound	PPN2	3a	3b	3c	5aFeCl ₄
Solvate	0.75 CH ₂ Cl ₂	—	—	—	0.4 THF · 0.5 Et ₂ O
Empirical formula (without solvate)	C ₉₅ H ₆₉ Cr ₃ FeN ₄ O ₁₅ P ₅	C ₅₄ H ₃₉ Cr ₂ FeN ₂ O ₁₁ P ₃	C ₆₂ H ₄₉ Cr ₂ F ₆ FeN ₂ O ₅ P ₃	C ₆₀ H ₅₃ FeMn ₂ N ₂ O ₅ P ₃	C ₁₀₀ H ₇₈ Cl ₄ Fe ₃ Mn ₃ N ₆ O ₁₂ P ₆
Molecular mass [g/mol]	1873.3	1144.5	1268.8	1140.7	2215.8
Crystal size [mm]	0.30×0.10×0.05	0.10×0.15×0.15	0.15×0.25×0.12	0.15×0.20×0.20	0.25×0.10×0.03
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
Lattice constants:					
<i>a</i> [pm]	1438.3(3)	1342.9(3)	1308.5(3)	1307.3(3)	2076.5(4)
<i>b</i> [pm]	1449.1(3)	2255.0(5)	2252.5(5)	2211.1(4)	2459.7(5)
<i>c</i> [pm]	2198.7(4)	1717.8(3)	1863.7(4)	1802.4(4)	2250.3(5)
<i>α</i> [°]	90	90	90	90	90
<i>β</i> [°]	95.31(3)	92.01(3)	91.12(3)	90.42(3)	114.64(3)
<i>γ</i> [°]	90	90	90	90	90
<i>V</i> [10 ⁶ ·pm ³]	4563.00	5198.70	5492.00	5209.80	10447.00
<i>Z</i>	2	4	4	4	4
<i>d_x</i> [g·cm ^{−3}]	1.410	1.462	1.535	1.454	1.455
<i>T</i> [K]	200	200	200	200	200
Scan range	3.4° ≤ 2θ ≤ 52.0°	3.0° ≤ 2θ ≤ 52.1°	2.8° ≤ 2θ ≤ 52.1°	2.9° ≤ 2θ ≤ 52.0°	3.5° ≤ 2θ ≤ 50.0°
Method	ω-Scan, Δω = 2.0°	ω-Scan, Δω = 1.0°	ω-Scan, Δω = 1.0°	ω-Scan, Δω = 1.0°	ω-Scan, Δω = 1.0°
Scan speed	18 s/frame	10 s/frame	10 s/frame	10 s/frame	30 s/frame
No. of measured reflections	70626	71226	89959	84087	162573
No. of unique reflections	17826	10221	10815	10254	18392
No. of observed reflections	11825	5734	8611	7205	9339
Observation criterion	<i>I</i> ≥ 2σ	<i>I</i> ≥ 2σ	<i>I</i> ≥ 2σ	<i>I</i> ≥ 2σ	<i>I</i> ≥ 2σ
No. of params. refined	987	662	734	525	1155
Resid. el. density [10 ^{−6} e·pm ^{−3}]	0.91	0.53	0.40	1.52	1.41
<i>R</i> ₁ / <i>R</i> _w [%] (refinement on <i>F</i> ²)	6.0/13.1	5.2/8.7	3.5/8.5	6.2/16.7	7.9/22.9

ite-monochromated Mo-*K*_α radiation). The data were processed by the standard Nonius software.^[23] All calculations were performed using the SHELX software package. Structures were solved by direct methods using the program SHELXS-97^[24] and refined using the program SHELXL-97.^[24] Graphical handling of the structural data during solution and refinement was performed with XPLA.^[25] Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least-squares calculations. Data relating to the structure determinations are compiled in Table 8. Figures 1, 2, and 3 were generated using WinRay-32 and WinRay-GL.^[26] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-156056 to -156060. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] [1a] S. Mann, G. Huttner, L. Zsolnai, K. Heinze, *Angew. Chem.* **1996**, 108, 2983; *Angew. Chem. Int. Ed. Engl.* **1996**, 35, 2808.
 — [1b] S. Mann, G. Huttner, L. Zsolnai, K. Heinze, V. Jacob,

B. Antelmann, A. Driess, B. Schiemenz, *Z. Naturforsch., Teil B* **2000**, 55, 638.

- [2] [2a] H. Krentzien, H. Taube, *Inorg. Chem.* **1982**, 21, 4001. — [2b] H. Krentzien, H. Taube, *J. Am. Chem. Soc.* **1976**, 98, 6379. — [2c] V. Jacob, S. Mann, G. Huttner, L. Zsolnai, O. Walter, E. Kaifer, P. Rutsch, P. Kircher, E. Bill, manuscript in preparation.
- [3] [3a] N. Zhu, H. Vahrenkamp, *J. Organomet. Chem.* **1999**, 573, 67; G. N. Richardson, H. Vahrenkamp, *J. Organomet. Chem.* **2000**, 593–594, 44; A. Geiß, H. Vahrenkamp, *Inorg. Chem.* **2000**, 39, 4029; A. Geiß, M. J. Kolm, C. Janiak, H. Vahrenkamp, *Inorg. Chem.* **2000**, 39, 4037; G. N. Richardson, U. Brand, H. Vahrenkamp, *Inorg. Chem.* **1999**, 38, 3070. — [3b] D. J. Darsensbourg, W.-Z. Lee, M. J. Adams, D. L. Larkins, J. H. Reibenspies, *Inorg. Chem.* **1999**, 38, 1378. — [3c] S. Bordoni, L. Busetto, P. Colucci, A. Palazzi, V. Zanotti, *J. Organomet. Chem.* **1997**, 545–546, 117.
- [4] N. Zhu, H. Vahrenkamp, *Chem. Ber./Recueil* **1997**, 130, 1241; H. Vahrenkamp, A. Geiß, G. N. Richardson, *J. Chem. Soc., Dalton Trans.* **1997**, 3643.
- [5] W. P. Fehlhammer, M. Fritz, *Chem. Rev.* **1993**, 93, 1243.
- [6] A. Gautier, *Justus Liebigs Ann. Chem.* **1867**, 142, 289; A. W. Hofmann, *Justus Liebigs Ann. Chem.* **1867**, 144, 115.
- [7] [7a] K. R. Dunbar, R. A. Heintz, *Prog. Inorg. Chem.* **1997**, 45, 283. [7b] R. B. King, *Inorg. Chem.* **1967**, 6, 25. — [7c] E. Bär, W. P. Fehlhammer, D. K. Breiting, J. Mink, *Inorg. Chim. Acta* **1984**, 82, L17.
- [8] [8a] M. Fritz, D. Rieger, E. Bär, G. Beck, J. Fuchs, G. Holzmann, W.-P. Fehlhammer, *Inorg. Chim. Acta* **1992**, 198–200, 513. — [8b] P. Braunstein, D. Cauzzi, D. Kelly, M. Lanfranchi, A. Tiripicchio, *Inorg. Chem.* **1993**, 32, 3373.
- [9] [9a] R. B. King, *Inorg. Chem.* **1967**, 6, 25 (1a[−]). — [9b] J. A. Dineen, P. L. Pauson, *J. Organomet. Chem.* **1974**, 71, 91–96 (1c[−]).
- [10] F. Bringewski, G. Huttner, W. Imhof, L. Zsolnai, *J. Organomet. Chem.* **1992**, 439, 33.

- [11] [11a] E. O. Fischer, R. J. J. Schneider, *J. Organomet. Chem.* **1968**, *12*, P27. – [11b] A. A. Ismail, I. S. Butler, G. Jaouen, *Inorg. Synth.* **1989**, *26*, 31 (**1b**[−]).
- [12] [12a] F. E. Kühn, I. S. Gonçalves, A. D. Lopes, J. P. Lopes, C. C. Romão, W. Wachter, J. Mink, L. Hajba, A. J. Parola, F. Pina, J. Sotomayor, *Eur. J. Inorg. Chem.* **1999**, 295 (**1a**[−]). – [12b] B. Oswald, A. K. Powell, F. Rashwan, J. Heinze, H. Vahrenkamp, *Chem. Ber.* **1990**, *123*, 243 (**1c**[−]).
- [13] A. Asam, B. Janssen, G. Huttner, L. Zsolnai, O. Walter, *Z. Naturforsch., Teil B* **1993**, *48*, 1707.
- [14] [14a] K. K. Klausmeyer, T. B. Rauchfuss, S. R. Wilson, *Angew. Chem.* **1998**, *110*, 1808; *Angew. Chem. Int. Ed.* **1998**, *37*, 1694. – [14b] K. K. Klausmeyer, S. R. Wilson, T. B. Rauchfuss, *J. Am. Chem. Soc.* **1999**, *121*, 2705. – [14c] S. M. Contakes, K. K. Klausmeyer, R. M. Milberg, S. R. Wilson, T. B. Rauchfuss, *Organometallics* **1998**, *17*, 3633.
- [15] [15a] W. Hieber, W. Schropp Jr., *Z. Naturforsch., Teil B* **1959**, *14*, 460; R. J. Angelici, *Inorg. Chem.* **1964**, *3*, 1099; M. F. Faroni, L. M. Frazee, N. J. Bremer, *J. Organomet. Chem.* **1969**, *19*, 225 (**4a**[−]); Y. Tang, J. Sun, J. Chen, *Organometallics* **1998**, *18*, 86. – [15b] C. E. Coffey, *J. Inorg. Nucl. Chem.* **1963**, *25*, 179 (**4b**[−]). – [15c] J. A. Dineen, P. L. Pauson, *J. Organomet. Chem.* **1974**, *71*, 77 (**4c**[−]).
- [16] Examples of pentanuclear complexes with similar geometry: [16a] K. Van Langenberg, S. R. Batten, K. J. Berry, D. C. R. Hockless, B. Moubaraki, K. S. Murray, *Inorg. Chem.* **1997**, *36*, 5006. – [16b] K. E. Vostrikova, D. Luneau, W. Wernsdorfer, P. Rey, M. Verdaguer, *J. Am. Chem. Soc.* **2000**, *122*, 1490.
- [17] C.-H. Lai, W.-Z. Lee, M. L. Miller, J. H. Reibenspies, D. J. Darensbourg, M. Y. Darensbourg, *J. Am. Chem. Soc.* **1998**, *120*, 10103 (**4b**[−]).
- [18] J. E. Sutton, P. M. Sutton, H. Taube, *Inorg. Chem.* **1979**, *18*, 1017.
- [19] C. Creutz, *Prog. Inorg. Chem.* **1983**, *30*, 1.
- [20] *Organikum*, Deutscher Verlag der Wissenschaften, Berlin, **1990**.
- [21] [21a] W. Hewertson, H. R. Watson, *J. Chem. Soc.* **1962**, 1490. – [21b] A. Muth, O. Walter, G. Huttner, A. Asam, L. Zsolnai, C. Emmerich, *Z. Naturforsch., Teil B* **1994**, *48*, 149.
- [22] H. Funk, F. Binder, *Z. Anorg. Allg. Chem.* **1926**, *155*, 327.
- [23] *DENZO-SMN*, Data processing software, Nonius, **1998**; <http://www.noniuss.com>
- [24] G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution*, University of Göttingen, **1997**; G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, **1997**; <http://shelx.uni-ac.gwdg.de/shelx/index.html>.
- [25] L. Zsolnai, G. Huttner, *XPLA*, University of Heidelberg, **1994**; <http://www.uni-heidelberg.de/institute/fak12/AC/huttner/htmlsoftware.html>
- [26] R. Soltek, G. Huttner, *WinRay-32*, University of Heidelberg, **1998**; R. Soltek, G. Huttner, *WinRay-GL*, University of Heidelberg, **2000**; <http://www.uni-heidelberg.de/institute/fak12/AC/huttner/htmlsoftware.html>

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