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Cyanide bridged trinuclear complexes with bent M–NC–Fe–CN–M and M–CN–Fe–NC–M arrangements—synthesis and physical properties[1]

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Abstract

Seven chain-like trinuclear complexes containing *cis*-configured central $Fe(CN)_2$ or $Fe(NC)_2$ units attached to two peripheral organometallic units containing Fe, Ru, Cr, or Mn have been synthesized. IR spectra and cyclic voltammograms allow assessment of their electronic situation. Chemical two-electron oxidations were possible for the complexes with $Fe(CN–Fe)_2$ backbones. The oxidized complexes give rise to metal–metal charge transfer bands indicative of significant metal–metal interactions. Their magnetic susceptibilities indicate the absence of magnetic coupling between their two unpaired electrons. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Trinuclear complexes; Cyanide bridging; Metal–metal charge transfer; Redox reactions

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1. Introduction

Finite molecular entities built up of metal complex units linked by cyanide ions have proven to possess physical properties as attractive as those of their infinite solid state counterparts, the best known of which is Prussian blue. They have been found to be suitable for electrical conduction [1], high magnetization [2], multi-step electron transfers [3], and light harvesting [4]. In a recent review [5] we have outlined the features and challenges offered by this class of compounds.

When scanning the literature [5] it became obvious to us that the numbers and types of polynuclear complexes with cyanide bridges investigated so far are still quite small, and even simple combinations of building blocks or molecular shapes have rarely been realized. Typical examples are cyanide/isocyanide (i.e. M–CN–M′ versus M–NC–M′) isomerism, trinuclear complexes with three different metals, and *cis*/*trans* phenomena, e.g. for $L_2Pt(CN–M)_2$ species. Each of these should have interesting physical consequences and hence deserve investigation.

So far we have synthesized and investigated two classes of cyanide linked oligonuclear complexes, those with cyanometal units linked to clusters [6] and chain-like arrangements [7,8]. This paper presents a contribution to the latter subject in the form of trinuclear complexes based on central $Fe(CN)_2$ units. The aim was to assess some basic electronic, redox, and magnetic properties for complexes with a bent $M(CN–M')_2$ arrangement containing a central atom M which is redox-active itself.

2. Syntheses and identifications

The two starting complexes with *cis*-configured $Fe(CN)_2$ units were compounds **1** and **2** which are

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[1] Dedicated to Professor B.F.G. Johnson on the occasion of his 60th birthday.

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easily accessible [9,10] and sufficiently inert towards cyanide displacement.

$K|FeCp(CO)(CN)_2|$ **1** $(bpy)_2Fe(CN)_2$ **2**

Treatment of **1** with two equivalents each of $[Cp(CO)_2Fe(THF)]BF_4$, Cp(dppe)FeBr, and $Cp(PPh_3)_2RuCl$ in methanol yielded the ionic trinuclear complexes **3**, **4** and **5** in moderate to good yields. They are of yellow to red colour and thermally stable except for **3** which cannot be stored for extended periods at room temperature.

$[L_nM–NC–FeCp(CO)–CN–ML_n]$ X

3: $ML_n = FeCp(CO)_2$, $X = BF_4$

4: $ML_n = FeCp(dppe)$, $X = PF_6$

5: $ML_n = RuCp(PPh_3)_2$, $X = PF_6$

In the same way reactions of **2** were possible with Cp(dppe)FeBr and $Cp(PPh_3)_2RuCl$. The resulting complexes **6** and **7** which are purple were obtained in quite good yields.

cis-$[L_nM–NC–Fe(bpy)_2–CN–ML_n]$ $(PF_6)_2$

6: $ML_n = FeCp(dppe)$

7: $ML_n = RuCp(PPh_3)_2$

Two neutral complexes with an inverted orientation of the cyanide ligands at the central iron atom could be obtained by using organometallic cyanides as reagents. We found to our surprise that $[Cr(CO)_5CN]^-$ and $[MnCp(CO)_2CN]^-$ can replace one bipyridine ligand from $[Fe(bpy)_3]^{2+}$ in aqueous solution, forming the purple complexes **8** and **9**, again in moderate to good yields.

cis-$[L_nM–CN–Fe(bpy)_2–NC–ML]$

8: $ML_n = Cr(CO)_5$

9: $ML_n = MnCp(CO)_2$

All trinuclear complexes **3**–**9** are diamagnetic and hence susceptible to NMR spectroscopy. In their ^{1}H-NMR spectra they show their predominantly aromatic constituents by multiplets in the aromatic region. In case of **3**, **4**, and **5** the 2:1 intensity ratio of the two Cp resonances confirmed the constitutional assignments. Likewise the ν(CO) absorptions in the IR spectra confirm the presence of $FeCp(CO)_2$, $Cr(CO)_5$, and $MnCp(CO)_2$ units in **3**, **8**, and **9** (see Section 5).

As usual for this type of complexes, the ν(CN) band positions yield significant bonding information. Table 1 lists the data for **3**–**9** and some reference compounds. As a rule the two ν(CN) absorptions are either very close to each other or not separated at all. Upon formation of the CN bridges the ν(CN) bands move by 20–40 cm^{-1} to higher wavenumbers compared to those of the corresponding mononuclear complexes. This phenomenon which results primarily from a kinematic effect and secondarily from strengthening the CN bond by using antibonding σ^* electrons for M–N coordination has been discussed many times [11]. In the present case it is noticeable that among the $Cp(CO)Fe(CN)_2$ based complexes it distinguishes **3** from **4** and **5**, the higher ν(CN) values for **3** reflecting the stronger electron accepting power of the terminal $FeCp(CO)_2$ units compared to $MCp(PR_3)_2$ in **4** and **5**. Furthermore the relative increase of ν(CN) within the pair **6**/**7** and the pair **8**/**9** is similar when compared to the mononuclear reference compounds **2** and $[L_nM–CN]^-$ indicating that the orientation of the cyanide bridge and the difference of two units in overall charge are of little influence here.

Table 1
ν(CN) IR bands (KBr, cm^{-1})

Complex	ν(CN)
$[Cp(CO)Fe(CN)_2]^-$	2099
$(bpy)_2Fe(CN)_2$	2069, 2079
$[(CO)_5CrCN]^-$	2096
$[Cp(CO)_2MnCN]^-$	2061
3	2132, 2141
4	2105, 2137[a]
5	2108, 2117[a]
6	2094
7	2090
8	2125
9	2051, 2076

[a] No band splitting observed in CH_2Cl_2 solution.

3. Redox properties

Except for **3** and **9** which decomposed too quickly, the trinuclear complexes yielded good cyclic voltammograms in dichloromethane solution. Table 2 lists the data. Their interpretation is straightforward. The first

Table 2
Cyclic voltammetry of the trinuclear complexes and some reference compounds (in CH_2Cl_2 with 0.1 M Bu_4NClO_4, scan speed 100 mV s^{-1}, half-wave potentials in V, reference Ag/AgCl)

Complex	Ox(1)	Ox(2)	Ox(3)
Cp(dppe)Fe-CN	0.48		
$Cp(PPh_3)_2Ru$-CN	0.79		
$[(CO)_5Cr–CN]^-$	0.58		
$(bpy)_2Fe(CN)_2$	0.46		
4	0.35 (2e)		
5	0.79	0.97	
6	0.35 (2e)		1.45
7	0.83	1.07	
8	0.56	0.87 (irr.)	

oxidation waves are assigned to the terminal organometallic units. Their potentials are close to those of the mononuclear reference compounds. Typically the $Cp(PR_3)_2Ru$ unit is much more difficult to oxidize than the $Cp(PR_3)_2Fe$ unit, and oxidation of the $(CO)_5Cr$ unit tends to be irreversible. The oxidations of the two terminal iron fragments in **4** and **6** seem to occur at the same potential while there is a small potential separation for **5** and **7** with terminal ruthenium fragments. In case of **6** which has the easiest first and second oxidations, the third oxidation, assignable to the central $Fe(bpy)_2$ unit, is also observed as a reversible wave at rather high potential.

The two complexes with the lowest redox potentials, **4** and **6**, could also be chemically converted to the doubly oxidized complexes **10** and **11**. The oxidant was ferrocenium hexafluorophosphate providing also the anions for **10** and **11**. Attempts to achieve one-electron oxidations failed. Using one equivalent of $[FeCp_2]PF_6$ produced mixtures of non-oxidized (**4**, **6**) and doubly-oxidized (**10**, **11**) compounds.

$[Cp(dppe)Fe–NC–FeCp(CO)–CN–Fe(dppe)Cp]\ (PF_6)_3$
10

$[Cp(dppe)Fe–NC–Fe(bpy)_2–CN–Fe(dppe)Cp]\ (PF_6)_4$
11

$[Cp(PPh_3)_2Ru–NC–Fe(bpy)_2–CN–Ru(PPh_3)_2Cp]^{n+}$
$n = 3$: **12a**, $n = 4$: **12b**

Chemical instability prevented the isolation of oxidation products of the ruthenium-containing complexes **5** and **7**. Optical spectroscopy (see below), however, indicated, that single and double oxidation of **7** is possible, as was to be expected from the clear separation of its first two redox potentials. We therefore assign the constitutions **12a** and **12b** to the one- and two-electron oxidation products obtained from **7** in solution.

The ν(CN) IR bands of the oxidized complexes are again quite indicative of their bonding situation. In KBr they are observed at 2090 and 2059 cm^{-1} for **10** and at 2065 and 2037 cm^{-1} for **11**. This corresponds to shifts of 30–60 cm^{-1} to lower wavenumbers in comparison to the non-oxidized precursors **4** and **6**. At the same time the intensities of the ν(CN) bands rise by a factor of more than ten, reflecting the increased polarity across the C≡N bond. These phenomena have been observed before [8,12]. They reflect a net flow of electron density from the cyanide C-bound central Fe unit towards the N-bound oxidized Fe(dppe)Cp unit. The corresponding increase in π-backdonation from the C-bound iron unit reduces the strength of the C≡N bond and hence ν(CN).

4. Metal–metal interactions

Cyclic voltammetry (see above) has given conflicting information with respect to the question whether there is electronic communication along the cyanide-linked chain of metal atoms. While the two terminal Fe(dppe)Cp units in **4** as well as in **6** are both oxidized at the same potential indicating their electronic independence, the two $Ru(PPh_3)_2Cp$ units in **5** and **7** seem to communicate, as the oxidation at one end of the RuFeRu chain seems to raise the potential for oxidation at the other end. This was somewhat surprising as we had expected (and observed in other cases [13]) that the electronic communication between the organometallic termini would be inhibited by the *cis*-configuration at the central $Fe(CN)_2$ unit [14,15]. We therefore collected further data to address this question.

Table 3
Electronic spectra of oxidized trinuclear complexes and their precursors (measured in acetone, λ in nm, ε in L M^{-1} $cm^{-1} \times 10^{-3}$)

Complex	MMCT λ (ε)	MLCT λ (ε)	Other λ (ε)
4			490 (3.4)
10	749 (2.6)		460 (3.6)
6		564 (5.1)	372 (6.7)
11	988 (4.4)	462 (5.3)	<330
7		560 (4.8)	364 (6.2)
12a	2080	470	<330
12b	1470	450	<330

The magnetic susceptibilities of the oxidized complexes **10** and **11**, measured at room temperature on a Faraday balance and corrected for diamagnetism, are 2.55 and 2.59×10^{-3} cm^3 mol^{-1}, respectively. This translates into 1.73 and 1.74 Bohr magnetons, respectively, per one paramagnetic Fe(dppe)Cp unit, i.e. the normal values for species with one unpaired electron. Thus the two paramagnetic centers each in **10** and **11** are magnetically independent at least at room temperature, and the results of the magnetic measurements speak against an electronic communication between them.

That there is electronic interaction across at least one CN linkage, is obvious from the UV/Vis/NIR spectra of the oxidized complexes. Table 3 lists the data. Representative spectra of the complex pair **6**/**11** are given in Fig. 1.

All three trinuclear complexes give rise to intense bands in the NIR region after oxidation, which must be assigned to metal–metal charge transfer. For the doubly oxidized complexes **10** and **11** the charge transfer is undoubtedly from the central L_nFe unit to the outer iron atoms, i.e. across one CN link. This is in accord with the MMCT band positions: the central $Fe(bpy)_2$ unit in **11** is easier to oxidize than the FeCp(CO) unit in **10**. At the same time the MLCT ($Fe^{2+} \rightarrow$ bpy) transition in **11** due to the oxidation requires more energy than that in **6**. While there is no such MLCT transition in **4** and **10**, the other electronic transitions in **4** and **6** also require more energy after oxidation to **10** and **11**.

All these observations are equivalent to those made before for similar dinuclear complexes.

The electronic spectra of the purported complexes **12a** and **12b** are consistent with the constitutions proposed. For doubly oxidized **12b** there is a similar shift of λ(MLCT) and λ(other) relative to the bands of **7** as for the complex pair **6**/**11**. The MMCT transition of **12b** requires less energy than that of **11** because the transition ends at a lower energy level in **12b**, cf. the first and second redox potentials of **6** and **7**. Most interesting is the MMCT band position of singly-oxidized **12a**. It has the lowest energy of all MMCT transitions recorded here. One possible explanation for this is that the MMCT actually takes place from the unoxidized to the oxidized ruthenium center. This is not unlikely since the first oxidation of one $Ru(PPh_3)_2Cp$ unit occurs easier than that of the $Fe(bpy)_2$ unit, cf. Table 2. However, since neither **12a** nor **12b** have been isolated or otherwise identified these assignments can only be tentative.

In summary it can be stated that the use of low spin complexes and substitution-inert organomeatllic building blocks has again facilitated the isolation and characterization of cyanide-bridged oligonuclear complexes. Their physical, specifically metal–metal charge transfer, properties are as attractive as those of their classical complex counterparts [5]. Their metal–metal interactions across the cyanide bridges, possibly over more than one CN linkage, have been demonstrated. They require the comparison of these *cis*-oriented $M(CN-M')_2$ systems with the corresponding *trans*-oriented counterparts and with longer-chain systems. Synthetic and physicochemical work in this direction is in progress.

5. Experimental

All preparative and measurement techniques and the synthesis of the starting compounds were as described before [8–10]. IR spectra were taken from KBr pellets, ^1H-NMR spectra were recorded in $CDCl_3$.

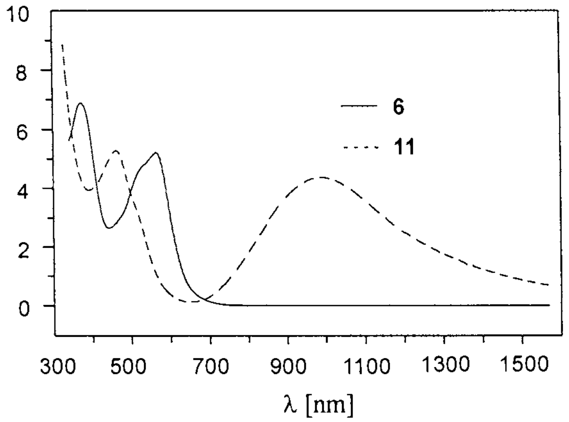

Fig. 1. UV/Vis/NIR spectra of **6** and **11**.

3: To a mixture of **1** (0.048 g, 0.20 mmol) and two equivalents of $[CpFe(CO)_2(THF)](BF_4)$ (0.134 g, 0.40 mmol) was added 15 ml of CH_3OH and the solution stirred for 24 h. Then 0.060 g (0.37 mmol) of NH_4PF_6 was added and the solution stirred for 10 min. The solvent of the resulting solution was removed under reduced pressure. The residue was extracted with 4 ml of CH_2Cl_2 and filtered. The filtrate was layered with 10 ml of isopropanol. The mixture was kept at 5°C for one day and a small amount of a microcrystalline precipitate was formed. The mixture was filtered and the filtrate layered with 20 ml of hexane. The mixture was kept again at 5°C for 2 days. After filtration, washing twice with 5 ml of hexane and drying under vacuum, 0.070 g (50%) of **3** as long needle-like yellow crystals were obtained, which are sensitive to air and light.

Anal. Found: C, 37.92; H, 2.12; N, 4.23. $C_{22}H_{15}F_6Fe_3N_2O_5P$ (699.88) Calc.: C, 37.75; H, 2.16; N, 4.00. IR: 2141m, 2132m (CN), 2061s, 2020s, 2007s, 1982m, 1969m (CO), 1038s (BF_4). ^1H-NMR: 5.20 (10H, Cp), 4.59 (5H, Cp).

4: To a mixture of **1** (0.033 g, 0.14 mmol), CpFe(dppe)Br (0.160 g, 0.27 mmol) and NH_4PF_6 (0.023 g, 0.14 mmol) was added 20 ml of CH_3OH and the mixture stirred for 2 h. The solvent of the resulting red solution was removed under reduced pressure. The residue was extracted with 10 ml of CH_2Cl_2 and then filtered. The filtrate was concentrated to 4 ml and 15 ml of isopropanol added. Red crystals were formed by slow evaporation of CH_2Cl_2 into pure isopropanol under reduced pressure at −27°C. After filtration, washing twice with 5 ml of hexane and drying under vacuum, 0.154 g (78%) of **4**·CH_2Cl_2 as red crystals were obtained.

Anal. Found: C, 58.94; H, 4.54; N, 1.89. $C_{71}H_{65}Cl_2F_6Fe_3N_2OP_5$ (1469.62) Calc.: C, 58.03; H, 4.46; N, 1.91. IR: 2137w, 2105m (CN), 1955s (CO), 840vs (PF_6). ^1H-NMR: 8.2–7.8 (m, 20H, Ph), 4.22 (10H, Cp), 3.53 (5H, Cp), 2.85–2.75 (m, 4H, C_2H_4).

5: To a mixture of **1** (0.120 g, 0.50 mmol) and $CpRu(PPh_3)_2Cl$ (0.730 g, 1.0 mmol) was added 15 ml of CH_3OH and the mixture warmed to 50°C in an oil bath. After a few minutes a clear yellow solution was formed. By addition of NH_4PF_6 (0.200 g, 1.2 mmol) a yellow precipitate was formed. After stirring for 15 min the solvent was removed under reduced pressure. The residue was extracted with 8 ml of CH_2Cl_2 and layered with 40 ml of isopropanol. The mixture was kept at room temperature for 3 days. After filtration, washing with 5 ml of isopropanol and then 5 ml of hexane, and drying under vacuum, 0.26 g (33%) of **5**·CH_2Cl_2 as needle-like yellow crystals were obtained.

Anal. Found: C, 60.42; H, 4.45; N, 1.56. $C_{91}H_{77}Cl_2F_6FeN_2OP_5Ru_2$ (1812.37). Calc.: C, 60.31; H, 4.28; N, 1.55. IR: 2117w, 2108m (CN), 1983s (CO), 840s (PF_6). ^{1}H-NMR: 7.3–7.0 (m, 30H, Ph), 4.19 (10H, Cp), 3.94 (5H, Cp).

6: To a mixture of **2**$\cdot 3H_2O$ (24 mg, 0.051 mmol) and CpFe(dppe)Br (60 mg, 0.10 mmol) was added 15 ml of CH_3OH and the mixture stirred overnight. Then NH_4PF_6 (40 mg, 0.25 mmol) was added and the solution stirred for 10 min. The solvent was removed under reduced pressure. The violet residue was extracted with 6 ml of CH_2Cl_2 and filtered. The filtrate was layered with 20 ml of Et_2O and kept at room temperature for one day. After filtration, washing twice with 5 ml of diethyl ether and drying under vacuum, 64 mg (73%) of **6** as needle-like violet crystals were obtained.

Anal. Found: C, 56.80; H, 4.32; N, 4.84. $C_{84}H_{74}F_{12}Fe_3N_6P_6$ (1748.92). Calc.: C, 57.69; H, 4.26; N, 4.81. IR: 2094w (CN), 841s (PF_6).

7: To a mixture of **2**$\cdot 3H_2O$ (24 mg, 0.051 mmol) and $Cp(Ph_3P)_2RuCl$ (75 mg, 0.10 mmol) was added 15 ml of CH_3OH and the mixture refluxed for 3 h. After cooling to room temperature NH_4PF_6 (25 mg, 0.15 mmol) was added and the mixture stirred for 10 min. The solvent was removed under reduced pressure. The violet residue was extracted with 6 ml of CH_2Cl_2, layered with 20 ml of isopropanol and left at room temperature for one day. After filtration, washing twice with 5 ml of diethyl ether and drying under vacuum, 73 mg (73%) of **7** as needle-like violet crystals were obtained.

Anal. Found: C, 60.28; H, 4.05; N, 3.72. $C_{104}H_{86}F_{12}FeN_6P_6Ru_2$ (2091.67). Calc.: C, 59.72; H, 4.14; N, 4.02. IR: 2090w (CN), 842s (PF_6).

8: A red aqueous solution of $[(bpy)_3Fe]^{2+}$ was formed from $FeSO_4\cdot 7H_2O$ (66 mg, 0.24 mmol) and 2,2′-bipyridine (111 mg, 0.72 mmol) in 15 ml of H_2O. To this solution $Na[NCCr(CO)_5]$ (110 mg, 0.46 mmol) in 10 ml of H_2O was added dropwise while stirring. A red precipitate was formed. The red precipitate was filtered off, washed three times with 2 ml of H_2O and dried under vacuum. The residue was dissolved in 10 ml of acetone forming a violet solution and then layered with 10 ml of diethyl ether. The mixture was kept at 5°C for 2 days. After filtration, washing twice with 5 ml of diethyl ether and drying under vacuum, 110 mg (58%) of **8** as violet crystals were obtained.

Anal. Found: C, 47.60; H, 2.01; N, 10.29. $C_{32}H_{16}Cr_2FeN_6O_{10}$ (803.90). Calc.: C, 47.78; H, 2.00; N, 10.45. IR: 2125w (CN), 2059w, 1982w, 1921s, 1872s (CO).

9: A red aqueous solution of $[(bpy)_3Fe]^{2+}$ was formed from $FeSO_4\cdot 7H_2O$ (140 mg, 0.51 mmol) and 2,2′-bipyridine (236 mg, 1.51 mmol) in 50 ml of H_2O. To this solution $Na[NCMn(CO)_2Cp]$ (226 mg, 1.04 mmol) in 20 ml of H_2O was added dropwise while stirring. A red solution and a red precipitate were formed. The reaction mixture was extracted with 20 ml of CH_2Cl_2 for three times. The dark-green CH_2Cl_2 extracts were combined and dried overnight with anhydrous $MgSO_4$. The mixture was filtered and the solvent removed under reduced pressure to leave a dark-green residue. The residue was redissolved in 10 ml of DMF forming a violet solution and layered with 50 ml of isopropanol. The mixture was kept at 5°C for three days. After filtration, washing with 5 ml of isopropanol and then 5 ml of hexane and drying under vacuum, 250 mg (63%) of **9** as violet crystals were obtained.

Anal. Found: C, 55.83; H, 3.39; N, 10.94. $C_{36}H_{26}FeMn_2N_6O_4$ (772.36). Calc.: C, 55.96; H, 3.39; N, 10.88. IR: 2051m, 2076m (CN), 1914s, 1846s (CO).

10: To a solution of **4** (120 mg, 0.087 mmol) in 15 ml of CH_2Cl_2 was added solid $[Cp_2Fe]PF_6$ (57 mg, 0.17 mmol) with stirring. The color of the solution changed to black. After stirring for 30 min the resulting solution was filtered and the filtrate was layered with 30 ml of diethyl ether. The mixture was kept at 4°C overnight. After filtration, washing twice with 5 ml of diethyl ether and drying under vacuum, 140 mg (97%) of **10** as black microcrystals were obtained, which are slightly soluble in CH_2Cl_2 but very soluble in acetone or acetonitrile.

Anal. Found: C, 50.13; H, 3.95; N, 1.82. $C_{70}H_{63}F_{18}Fe_3N_2OP_7$ (1674.60). Calc.: C, 50.21; H, 3.79; N, 1.67. IR: 2090m, 2059s (CN), 2006m, 1995m (CO), 839vs (PF_6).

11: To a solution of **6** (172 mg, 0.10 mmol) in 15 ml of CH_2Cl_2 was added solid $[Cp_2Fe](PF_6)$ (67 mg, 0.20 mmol) with stirring. A dark brown solution was formed which gradually afforded a brown precipitate. The precipitate was filtered off, washed with 4 ml of CH_2Cl_2 and dried under vacuum. The residue was redissolved in 25 ml of acetonitrile and filtered. Cubic crystals were formed by slow diffusion of diethyl ether into the filtrate. After filtration, washing twice with 5 ml of diethyl ether and drying under vacuum, 130 mg (64%) of **11** as cube-like brown crystals were obtained.

Anal. Found: C, 48.27; H, 3.92; N, 3.85. $C_{84}H_{74}F_{24}Fe_3N_6P_8$ (2039.02). Calc.: C, 49.44; H, 3.63; N, 4.12. IR: 2065m, 2037s (CN), 840vs (PF_6).

Oxidation of **7**: Two solutions, each of 0.01 mmol of **7** in 5 ml of CH_2Cl_2, were treated dropwise with one and two equivalents, respectively, of a 0.01 M solution of $[(p\text{-}Br{-}C_6H_4)_3N]$ $(SbCl_6)$ (magic blue) in CH_2Cl_2. The blue colour of the oxidant disappeared. Electronic spectra were recorded immediately. Within about 1 h precipitation of decomposition products set in.

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