A bis(μ-isocyanide diiron) complex as chelating ligand towards iron(II), palladium(II), zinc(II) and cadmium(II). X-ray structural assessment of a novel isocyanide bridging mode

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Abstract

Reaction of 1,2-diisocyanobenzene with $[Fe_2Cp_2(CO)_3NCMe]$ (Cp = η-cyclopentadienyl) (1:2) yields the tetranuclear complex $[\{Fe_2Cp_2(CO)_2(\mu\text{-}CO)\}_2(\mu_4\text{-}CNC_6H_4NC)]$ (2) which in solution appears to exist as a mixture of *cis* and *trans* isomeric forms. 2 may be diprotonated to yield $[\{Fe_2Cp_2(CO)_3\}_2(\mu_4\text{-}CN(H)C_6H_4N(H)C)](BF_4)_2$ (3), mono-alkylated to give $[\{Fe_2Cp_2(CO)_3\}_2(\mu_4\text{-}CN(R)C_6H_4NC)]BF_4$ (R = Me (4), Et (5)) and oxidatively cleaved with one molecule of I_2 to give $[FeCp(I)(CO)_2]$ and the asymmetric species $[\{Fe_2Cp_2(CO)_3\}CNC_6H_4NC\{FeCp(I)CO\}]$ (6). In addition, 2 acts as a bidentate ligand towards the Lewis acidic metal halides $FeCl_2$, $PdCl_2$, $ZnCl_2$, ZnI_2 and CdI_2 giving rise to surprisingly stable pentanuclear supercomplexes (7a–e) which have been characterized by elemental analyses and IR and NMR (^1H, ^{13}C) spectra. Of 7c, an X-ray structure analysis has been carried out which for the first time assesses the μ_3-(C,C,N) bridging mode of isocyanide in a non-cluster molecule The most striking stereochemical features are the various gross distortions and deviations from more idealized geometries which are undoubtedly governed by the steric overcrowding in the molecule.

Introduction

Compared to the widespread occurrence of bridging carbonyl ligands, isocyanide bridges are much less abundant though well known in organometallic and cluster chemistry. With very few exceptions, they are all of the two electron donor 'upright' μ_2-type **A** [1] from which, however, some major deviations have been reported. Thus, rather unusual C–N–R and M–C–M angles have been found in the metal–metal bonded $[Pd_2Cl_2(CNC_6H_3Me_2\text{-}2,6)_2(py)_2]$ (**B**) [2] and the 'A-frame' species $[Pd_2(dppm)_2(CNMe)_3](PF_6)_2$ (**C**) [3] ('dimetalated ketimine' [4]), respectively, which at the same time exhibit particularly high or low CN bond orders as indicated by the ν(CN) IR frequencies (≈ 2000 (**B**) and 1650 (**C**) versus ≈ 1750 (**A**) cm^{-1} [1]). Two complexes, $[Mn_2(dppm)_2(CO)_4(\mu\text{-}\eta^2\text{-}CNC_6H_4Me\text{-}p)]$ [5] and $[Mo_2Cp_2(CO)_4(\mu\text{-}\eta^2\text{-}CNPh)]$ [6], have been described in which the isocyanide ligand bridges two metals in a σ,π-fashion (**D**) donating a total of four electrons; also, note that some members of the **D** family, e.g. the one with a bridging CN ligand, have attracted attention for their unique dynamics resembling a 'windshield wiper' motion [7]. Furthermore, there exist three versions of μ_3-CNR bridges in clusters: in one, **E**, CNR links two metals in the 'normal' (μ_2-(C,C)) way while binding to a third metal through the lone pair at the N atom; this structural motif is contained within the skeletons of $[Os_6(CO)_{18}(CNC_6H_4Me\text{-}p)_2]$ [8] and $[Pt_7(CNC_6H_3Me_2\text{-}2,6)_{12}]$ [9], and probably also of $[Ni_4(CNBu^t)_7]$** [10]. The second, **F**, forms six electron donor-CNR-bridged M_3 structures as in $[Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CNBu^t)]$ [11] or $[Nb_3Cl_8(CNBu^t)_5]$ [12] where the isocyanide is σ-bonded through C to one metal and π-bonded though the C≡N unit to the other two. Remarkably, through **A**–**F** (and **H**) point to an even richer variety in bridging modes of CNR than in those of CO, the common 'upright' (two electron) μ_3-η^1-CO capping of M_3 triangles has so far been accomplished with isocyanides in one case only (**G**) [13, 14]†.

The μ_5-bridge **H** in $[Ru_5(CO)_{14}(CNBu^t)_2]$ completes the list of CNR bridging modes which have been assessed by X-ray structure determinations [15].

**Due to a low crystal quality there is some uncertainty as to the exact nature of the isocyanide bridge in $Ni_4(CNBu^t)_7$.

†A tricobalt cluster with a heavily bent μ_3-isocyanide bridging ligand has been described by Fortune *et al.* [13] Note that $(OC)_5CrCNC[Co(CO)_3]_3$ has been described as a 'permetalated methylisocyanide' which is further coordinated to chromium [14]. Thus, the cluster contains a μ_3-(isocyano)methylidyne and *not* a μ_3-isocyanide bridge as has falsely been gathered at first glance

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A

B

C

D

E

F

G

H
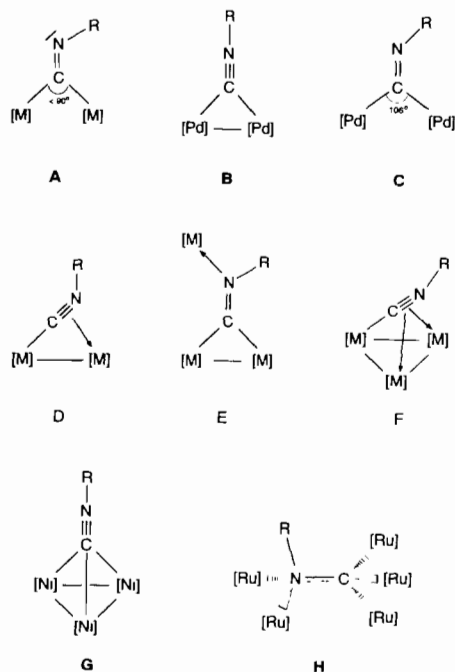
In 1982, Manning *et al.* reported on rather labile and poorly characterized Lewis acid adducts to the N atoms of the μ_2-CNR ligands in complexes of the general formula $[Fe_2Cp_2(CO)_{4-n}(CNMe)_n]$ ($n = 1, 2$) [16]; earlier, N-protonations, -alkylations and -acylations had been carried out which established the markedly basic nature of this nitrogen [17].

In the course of our investigations of neighboring group effects in metal complexes of ortho-functional isocyanides of the type **1a,b** [18], we have coordinated both isocyano groups of **1a** to $[Fe_2Cp_2(CO)_3]$ fragments. In the tetranuclear product **2** they occupy bridging positions resulting in two bent CNC arrays with basic sp²-N atoms which, in the proper conformation, suggest the use of **2** as a ligand for metal chelation. Here we report on the syntheses and characterizations of **2** and a number of pentanuclear chelates including an X-ray structure analysis of one sample which for the first time assesses the μ_3-(C,C,N) CNR bridging mode **E** outside a cluster.
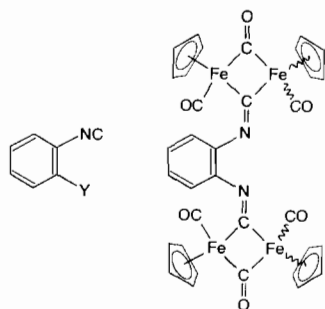
(Y = NC (**1a**), N₃(**1b**))   **2**

Results and discussion

The 'ligand'. Protonation studies

On addition of half an equivalent to the diisocyanide **1a**, the green solution of *in situ* prepared $[Fe_2Cp_2(CO)_3NCMe]$ in acetonitrile turned red–brown immediately; work-up including chromatography then gave the violet crystalline complex **2** in a 26% yield. The presence in the IR spectrum of **2** both in the solid state and in solution of only a weak band at *c.* 2090 cm^{-1} as compared to the very strong band at 1675 cm^{-1} shows that **2** exists mainly in the μ_2-CNR bridged form. Also, the solution spectrum in 1,2-dimethoxyethane remained essentially unchanged over the temperature range from 0 to 85 °C (Table 1). This is in fact not unexpected as arylisocyanide derivatives of $[FeCp(CO)_2]_2$, contrary to the alkylisocyanide and -diisocyanide analogues, strongly prefer the isocyanide in the bridging position [19, 20]. In the ¹H NMR spectrum in CDCl₃, however, two Cp signals appear at 4.76 and 4.88 ppm having an intensity ratio of 1:1.2 which changes to about 1:3.5 in the more polar solvent DMSO. Warming the DMSO solution to 310 K made the signals coalesce, and this process proved reversible on cooling to 290 K (Table 2). The only plausible explanation is some sort of *cis–trans* interconversion which, according to the Adams-Cotton mechanism, requires bridge ⇔ terminal CNR and CO ligand exchange at the same time. From similar observations, the presence of *cis* and *trans* isomers in solvent-dependent proportions has also been gathered for $[Fe_2Cp_2(CO)_3CNPh]$ and some methyl-substituted derivatives thereof [21]. With more bulky aryl groups, isomers with terminal isocyanide ligands, too, were detectable [22].

In the ¹³C NMR spectrum of **2** — unlike in that of $[Fe_2Cp_2(CO)_3CNPh]$ — only one set of signals was found, i.e. *cis*, *trans* differentiation was not observed (Table 3).

(BF₄)₂

3
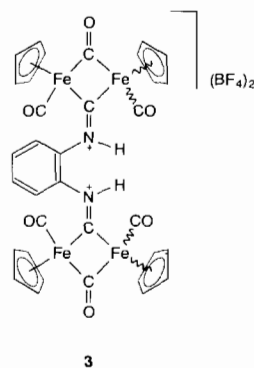
Protonation of **2** with HBF₄ in excess gave rise to the dicationic salt **3** which also appears to exist in mixtures with unreacted **2** if only one equivalent of acid (or less) was applied. In this respect, the reaction

TABLE 1. Selected IR data (cm^{-1})

Complex	Solvent	ν(NH)	ν(CN$_t$)	ν(CO$_t$)	$\nu(\mu$-CO)	$\nu(\mu$-CN)	$\nu(\mu$-C=N$^+$<)
2	CH$_2$Cl$_2$		2094w	1987vs, 1946vs	1787s, 1746s	1675vs	
	Glyme[a]		2090w	1982s, 1943s	1792s, 1751m	1674vs	
	Nujol		2091w	1986vs(br)	1789vs, 1747m	1656vs(br)	
	KBr		2090w	1982vs, 1940vs	1790s, 1745s	1667vs	
3	Nujol	3177w		2022vs, 1988s	1835vs		1512m, 1494m
	KBr	3166w		2020vs, 1995s	1832s(br)		1510m, 1500m
4	Nujol			2020s, 1981vs, 1944m	1829s, 1789m	1653s	1537m
	KBr			2018s, 1981vs, 1942m	1827s, 1789s	1653vs	1538m
5	Nujol			2019s, 1980vs	1832s, 1789m	1651s	1525m
	KBr			2017s, 1981vs, 1943m	1828s, 1789s	1651s	1527m
6	CH$_2$Cl$_2$		2124s	1984vs, 1947m	1785s	1661s(br)	
	KBr		2131s	1992vs, 1977vs, 1938m	1791s	1663s	
7a	Nujol			1992m, 1973vs, 1958m	1814s, 1799s		1530m, 1509s
7b	KBr			2007vs, 1962m	1809vs		1536m, 1518s
7c	CH$_2$Cl$_2$			1986sh, 1971vs	1809s		1534s, 1514s
	KBr			2004m, 1970vs(br)	1802s, 1789s		1533m, 1506s
7d	CH$_2$Cl$_2$			1995m, 1971vs	1810s		1530m, 1510m
	KBr			1994s, 1975vs, 1953vs	1793vs		1534s, 1512m
7e	CH$_2$Cl$_2$			1987s, 1970vs	1809s		1536s
	Nujol			1992m, 1973s, 1954vs	1791vs		1530s

[a]Temperature range: 0 to +85 °C

is reminiscent of the protonation of [Fe$_2$(CN)Cp$_2$(CO)$_3$]$^-$ which, irrespective of the stoichiometry, yielded the diprotonated μ-CNH$_2$$^+$ complex [23]. Only diprotonation products have also been reported of the 1,2-diisocyanoethane and 1,6-diisocyanohexane analogues [{Fe$_2$Cp$_2$(CO)$_3$}$_2$CN(CH$_2$)$_n$NC] (n = 2, 6) though, apparently, no efforts have been made to achieve monoprotonation in these cases [20]. A decrease of c. 150 wavenumbers of the CN stretching band on going from $\nu(\mu$-CNR) to $\nu(\mu$-CNHR$^+$) is consistent with the structure assigned to 3 as is the increase of c. 40 cm^{-1} in the symmetric and asymmetric ν(CO)$_t$ bands and of c. 70 cm^{-1} in $\nu(\mu$-CO). Similar shifts have previously been observed in protonation and alkylation reactions of related di- and tetranuclear isocyanide and diisocyanide bridged iron complexes [17, 20]. The positions (at c. 3180 and 1100, 1017 and 980 cm^{-1}, respectively), numbers and appearance of both the ν(NH) and the ν(BF$_4$) bands are indicative of extensive hydrogen bonding between the charged species [24]. This is further borne out by an extremely broad ^{1}H NMR signal for the NH species at c. 8–10 ppm in dimethyl sulfoxide (where there is some exchange with traces of water in the solvent) which moves to somewhere around δ 14.0 in acetone. While the small peaks between δ 4.8 and 5.1 must be due to Cp species of other (cis/trans; trans/trans?) isomers, the main Cp resonance of 3 is a singlet(!) of roughly 80% integrated intensity which lies at a slightly lower field (DMSO-d$_6$: 5.17 ppm) as compared to 2. Obviously, there is an accidental coincidence of

the signals of the non-equivalent Cps of the non-fluxional bis(μ-aminocarbyne) structure 3 which is partially removed in acetone, yet fully in the case of the chelate structures 7 (see 3 and Table 2).

Some decomposition — presumably partial deprotonation — of 3 is observed during the registration of the IR and, particularly, the ^{13}C NMR spectra. The value for the molar conductivity, too, is in a range characteristic for 1:1 electrolytes (see Table 5)! In the pos-FAB, expectedly, the monoprotonated cation (m/z 781) shows up with low intensity and is followed by plausible fragments ('Experimental').

Alkylation and oxidation studies

Preliminary alkylation studies, in contrast, point to an exclusive monoalkylation of 2, no matter which type and amount of alkylating agent was used. Steric reasons may be put forward for these findings. As expected, the IR spectra of the methylated and ethylated products 4 and 5 simply exhibit the sum of the bands of the bis(isocyanide)-bridged neutral complex 2 and the bis(aminocarbyne or 'iminium')-bridged dication 3 (Table 1). According to the ^{1}H and ^{13}C NMR spectra, however, at least two isomers, viz. the combinations of a cis-μ-carbynediiron entity with both, a cis- and a trans-μ-isocyanidediiron group must be present in 4 and 5 (Tables 2 and 3). More work (including X-ray) is needed to possibly separate the isomers and confirm the structural assignments [25].
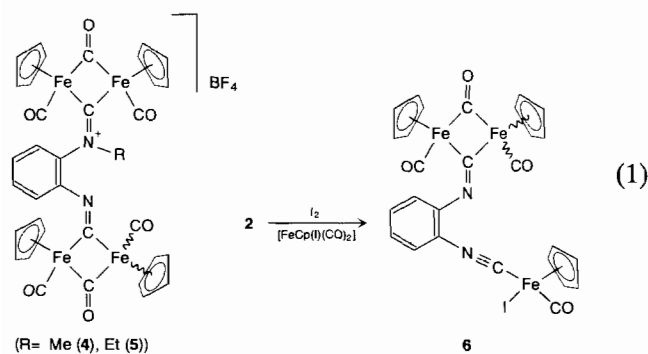
TABLE 2. ¹H NMR spectra of the complexes described in text[a]

| Complex	Solvent	C₆H₄	η-C₅H₅	CH₃	CH₂	NH
2	DMSO-d₆	7.08 (s, br, 2H), 7.28 (s, br, 2H)	290 K: 4 87 (s), 5.05 (s) [1.3.5]^b 310 K: 5.00 (s)			
3	CDCl₃ DMSO-d₆ Acetone-d₆	7.29 (m, br, 4H) 7.4–7.7 (m, 4H) 7.4–77 (m, 4H)	4.76 (s), 4.88 (s) [1:1 2] (4.8–5.1)^c, 5 17 (s) [1:4] 5.03 (s), 5.09 (s), 5 26 (s), 5.30 (s) [1:1·4:1]			8–10 (?)(2H) 13 84 (br, 2H)
4	DMSO-d₆	7.4–7.8 (m, 4H)	4.84 (s), 4.88 (s), 5.00 (s), 5.09 (s), 5.10 (s), 5.67 (s) [1:1·2.1:1:2]	4.60 (s), 4.64 (s) [1.4·1]		
5	DMSO-d₆	7 3–7.9 (m, 4H)	4.84(s), 4.86 (s), 5.02 (s), 5 10 (s), 5.64 (s), 5.66 (s)^d	1.42(t), 1 68(t) [1·1]	c. 4.9 (m, br)	
6	DMSO-d₆ CDCl₃	7.01 (dd, 1H), 7.31 (t, 1H), 7.53 (dt, 1H), 7 80 (dd, 1H) 7 09 (d, 1H), 7.19 (t, 1H), 7.42 (t, 1H), 7.52 (d, 1H)	5.14 (s), 4.96 (s), 4.98 (s)^d 4.96 (s), 4.84 (s), 4 87 (s)^d			
7c	CDCl₃	7.48 (m, 2H), 7 90 (m, 2H)	4.64 (s), 5.22 (s) [1:1]			
7d	CDCl₃	7.49 (m, 2H), 7.88 (m, 2H)	4.64 (s), 5 25 (s) [1:1]			
7e	CDCl₃	7.50 (m, 2H), 7.83 (m, 2H)	4 66 (s), 5 22 (s) [1:1]			

[a]Chemical shifts, δ, as ppm downfield from Me₄Si as an internal standard. [b]Signal intensity ratio. [c]Several weak signals. [d]About equal intensity.

TABLE 3. Selected ¹³C NMR data[a]

Complex	Solvent	μ-C=N⁺<	μ-CO	μ-CN	(CO)t	(CN)t	C₆H₄	η-C₅H₅	CH₃
2	DMSO-d₆		271.00	253.28	211 95		140 71, 124 17, 120 85	88.25	
3	DMSO-d₆	321.9br	268.56		211.20, 210.24^b		143.6–118 5^d	87.70, 87 50, 87.39, 85.35 [c. 1:2.2:1]	
4	DMSO-d₆	324.61	269.50, 268 53 267.30, 265 28^b	256.04 254.82^b	212.05, 210 74 209.35, 207.04^c		140 9–120.8^d	90.93, 90 44, 89 80, 88.72, 88.18, 87 68^e	
6	DMSO-d₆		269.24	263 87	218 24, 211 85, 211.67^b	171.48	144.50, 130.24, 127 99, 123 87, 120 91, 119.97	88 36, 88 57, 83.09^b	
7c	CD₂Cl₂	306 48	264 43		212.05, 209 68^b		140 99, 133 16, 131 32, 129.24, 127 10, 122.46	92 55, 90 49 [1:1]	
7e	CDCl₃	300 19	264.37		211.40, 209.33^b		139.91, 126 70, 122.98	91 90, 89.68 [1·1]	56 22

[a]Chemical shifts, δ, as ppm downfield from Me₄Si as an internal standard. [b]About equal intensities. [c]Additional peaks of ≈half intensity at 212 30, 211 16, 208.80, 207 94. [d]Six or more signals of comparable intensity. [e]Intensity ratio ≈1 5 1:3 2:1.2.

BF₄

(R= Me (4), Et (5))

(1)

$2 \xrightarrow[\text{[FeCp(I)(CO)}_2]]{I_2}$

6

7

	a	b	c	d	e
M	Fe	Pd	Zn	Zn	Cd
X	Cl	Cl	I	I	I

Action of one equivalent of iodine on **2** cleanly removes one iron fragment from the tetranuclear array leaving a '1,2-diisocyanobenzene' (**6**) in an asymmetric terminal/bridge bonding situation which is in full agreement with the spectroscopic and analytical data (eqn. (1) and Tables 1–3, 5). Unlike in our amine additions to (μ-1,2-diisocyanobenzene)-bis(chlorogold) [18], the expected ring closure by nucleophilic attack of the μ-CNR nitrogen at the CNR_t carbon to give a benzimidazole species bonded to the three iron atoms in a μ-carbyne/terminal-carbene fashion (**I**) did not occur, however.
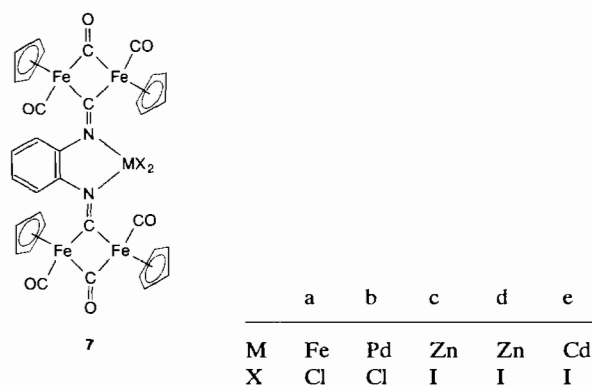
C—FeCp(I)CO

I
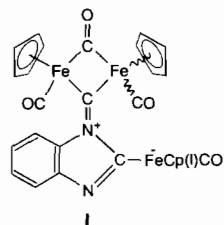
Pentametal arrays

In this paragraph, we show that 1,2-diisocyanobenzene acts as a twofold bridging plus chelating ligand towards four iron(I) and a fifth two-valent metal atom including Fe(II). In a typical experiment, a binary metal(II) halide or a nitrile complex is suspended in a solution of **2** in CH_2Cl_2; within a few hours, the color of the mostly heterogeneous mixture then changes from burgundy to cherry-red, and the product separates after layering with petrolether as micro-crystalline material which is already analytically pure (see Table 5). No special features such as a particularly intense color are encountered in the case of the mixed-valence compound **7a**.

Thanks to their chelate nature, the polynuclear metal complexes **7a–e** are stable enough for their IR and ¹H NMR spectra to be recorded, while extensive decomposition into the constituents **2** and MX₂ occurred in DMSO solution during the ¹³C NMR data collection*.

In chlorinated hydrocarbon solvents, however, full sets of reasonable ¹³C resonances could be obtained for **7c** and **e** which nicely correlate with those of **3**. The observed and well resolved Cp (¹H, ¹³C) and CO_t doublets are the minimum number of signals required for the rigid chelate structures of **7** which possibly exist in one isomeric form (*trans/trans*(?), see below) only, even in solution**. The shifts in the δ values of the bridging carbon atoms on going from the bis(μ_2-isocyanide) (**2**: 253.3 [CN], 271.0 [CO] ppm) to the bis-(μ_3-iminomethylene) systems (**7c, e**: $\approx$305 [CN], 264 [CO] ppm) are considerably smaller than those reported by Howell and Rowan for their diisocyanoalkane analogues and protonation products [20], yet point in the same direction (Table 3).

'Dimer scission' — a major pathway of decomposition in Manning's studies of adduct formation [16, 26] — was of no account in this investigation.

X-ray structure of 7c

The discrete molecule of **7c** has the expected supercomplex structure in which a diisocyanide tetrairon entity acts as a bidentate ligand toward zinc(II) (Fig. 1). The 'bite' of **2** is small constraining the N1–Zn–N2 angle to only 82.4(3)° — which is a reduction of 27.1° (!) from the normal sp³ tetrahedral angle, but similar values have been found in complexes of related bidentate ligands such as 1,10-phenanthroline (ZnCl₂(phen): 80.4(3)° [27], ZnCl₂(2,9-Me₂phen): 81.5(3)° [28]), 2,2-bipyridyl (ZnCl₂(bipy): 80.3(1)° [29]) or 1,4-diaza-1,3-butadienes [30] — and the whole arrangement is quite rigid which presumably causes the various distortions and deviations of the structure from higher symmetries. A particularly heavily distorted stereochemistry with

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*For a rationalization of the much higher stability of our Lewis acid adducts to the μ-CNR ligand as compared to those of Manning (cf. ref. 16) it should be recalled that his 1:1 adducts are not only non-chelates but also coordinatively unsaturated.

One referee pointed out, that the largely insoluble palladium adduct **7b is likely to be more complex. However, the recently prepared 1,2-diisocyanoethane analogue is sufficiently soluble to obtain NMR spectra which match perfectly with those of other (μ_5-diisocyanide)tetrairon metal complexes: see ref. 33.
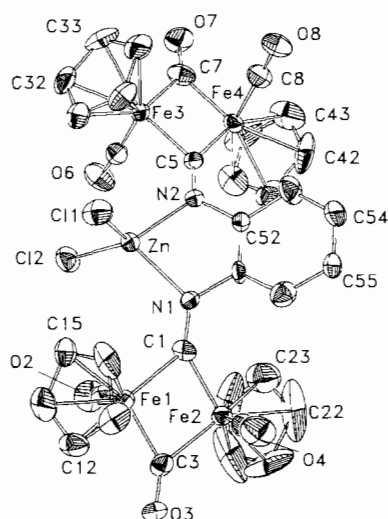
Fig 1 ORTEP plot and atom labelling scheme of **7c**. Hydrogen atoms have been omitted for clarity and the thermal ellipsoids have been drawn to include 50% probability.
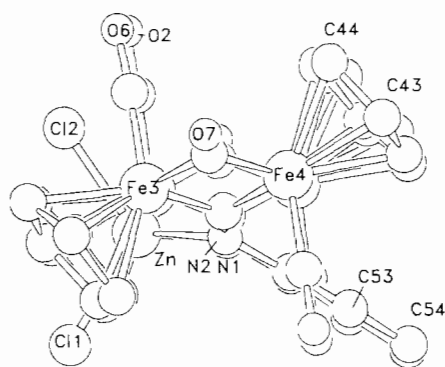

Fig. 2 SCHAKAL drawing of **7c** Projection of the molecule parallel to the benzene plane showing the molecular folding along the N1...N2 line and the dislocation of the $ZnCl_2N_2$ core with respect to the $[Fe]_4$ 'envelope'.

greatly discrepant Zn–Cl distances ($\Delta > 17\sigma$) [31]* and N–Zn–Cl angles along with an N1,Zn,N2//Cl1,Zn,Cl2 interplanar angle of only 67.3(2)° has been found around zinc which thus is far from being coordinated in a C_{2v}-pseudotetrahedral (*mm*) fashion (Table 4). The high asymmetry in the Zn–Cl bond lengths is further reflected in the H-bonding to a solvent molecule (CH_2Cl_2) in which, symptomatically, the chloro ligand (Cl1) with the longer bond to zinc is more strongly involved (Table 4). The most obvious effect of the overall steric crowdedness, however, is the unexpected pronounced non-planarity of the central five-membered metallacycle, despite its chain of four sp^2-hybridized C and N atoms.

A proper description of this non-planarity can be given in terms of a fold of 161.4(2)° along the N1...N2 vector which obviously serves the purpose of bending the benzene ring away from the Fe2Cp2 and Fe4Cp4 groups (Fig. 2). A molecular folding of exactly the same type and magnitude (163.3°) has been reported for the 1:1 adducts of *N,N,N',N'*-tetramethyl-*o*-phenylendiamine with zinc(II) and its mercury analogues and traced back to interactions between one halide ligand and nearby ligand methyl groups [32].

A further puckering (164.5(9)°) is observed in one of the four-membered Fe_2C_2 rings (Fe3Fe4C5C7), while the other one is perfectly planar thereby imposing a further asymmetry on the complex which is possibly maintained in solution showing up, for example, in the ^{13}C NMR spectra. Also notice that in contrast to most monosubstituted Fp_2 derivatives the configuration of both Fe_2C_2 rings in **7c** is *trans*. Apart from that, the

*Zn–Cl bond distances in tetrahedral $ZnCl_2L_2$ complexes (L = monodentate nitrogen donor) have been reviewed [31]

bonding parameters in these parts of the molecule are in the usual range [19].

From Fig. 2 and the interplanar angles in Table 4, finally, a severe 'bending back' of the two $Fe_2Cp_2(CO)_3$ fragments from an approximate plane through the chelate ring is evident; this way, the Cp rings above (C31–C35) and below (C11–C15) are as effectively moved out of the reach of the $ZnCl_2$ group as are the CO_t (C8O8, C4O4) ligands of the benzene ring.

It is absolutely made clear by these X-ray results that no more than one chelating ligand of type **2** will fit around a central Lewis acidic metal whatever coordination geometry (tetrahedral, square planar or some D_{2d} intermediate) is adopted; thus, neither homoleptic supercomplexes nor any tendency to polymer formation will be expected from this kind of metal–ligand interaction. For the same steric reasons, dimer formation through the approach of halide from a neighboring molecule as observed in $ZnI_2(o-Me_2NC_6H_4NMe_2)$ [32] can safely be ruled out. After all, from the ligand bulk coupled with the small bite and a moderate donor capacity one would predict only weak adducts with selected metal ions that easily dissociate into their components – in full accord with the experimental findings.

Interestingly, most of the shortcomings of **2** are overcome by the more flexible chelating ligand '[{$Fe_2Cp_2(CO)_3$}$_2$(μ_4-CNCH$_2$CH$_2$NC)]' the coordination chemistry of which will be discussed elsewhere [33].

Experimental

All manipulations were performed under an inert atmosphere of argon by using standard Schlenk and vacuum-line techniques. The solvents were deoxygenated and dried prior to use.

IR spectra were measured on a Perkin-Elmer 983 IR spectrophotometer and are summarized in Table 1.

TABLE 4. Selected inter- and intramolecular contact distances, bond distances (Å), bond angles, interplanar and dihedral angles (°)[a, b]

Intermolecular contact distances[c]

O4..H12[I]	2.48	C100...O7[II]	3.23(1)
H202...Cl1[II]	2.52	C45...C31[IV]	3 35(1)
O3...H54[III]	2.60	C22...O4[I]	3.36(3)
H102...O7[I]	2.66	O6...O6[I]	3.36(3)
H202..Cl11[II]	2.86	Cl11...O7[I]	3.390(8)
H101...Cl22[II]	3.15	C121...O4[I]	3.41(1)
		Cl1...C200[II]	3.53(2)

Intramolecular contact distances

Zn...H15	2 90	Zn...C15	3.51
Zn...H31	2.98	Zn...C31	3.51
Cl1...H35	2.90	Cl2...H15	2.95
Cl1...H15	2.95	Cl2 .H31	2.97
Cl1...C35	3.55	Cl2...O6	3.52
Cl1...C15	3.59	Cl2...C6	3.54
		Cl2...C2	3.56
		Cl2...O2	3.60

Bond distances

Zn–Cl1	2.242(3)	Zn–N1	2.085(7)
Zn–Cl2	2.190(3)	Zn–N2	2.068(7)
Fe1–Fe2	2 509(3)		
Fe1–C1	1.893(9)	Fe2–C1	1.901(8)
Fe1–C3	1.904(9)	Fe2–C3	1 942(10)
Fe1–C2	1.777(10)	Fe2–C4	1 754(10)
Fe1–C(Cp)[d]	2.104	Fe2–C(Cp)[d]	2.108
Fe3–Fe4	2.513(2)		
Fe3–C5	1.911(9)	Fe4–C5	1.902(8)
Fe3–C7	1.907(9)	Fe4–C7	1 913(10)
Fe3–C6	1.769(10)	Fe4–C8	1.780(10)
Fe3–C(Cp)[d]	2 106	Fe4–C(Cp)[d]	2.103
N1–C1	1.277(10)	N2–C5	1.268(10)
N1–C51	1.43(1)	N2–C52	1.43(1)
C2–O2	1.13(1)	C6–O6	1.14(1)
C3–O3	1.16(1)	C7–O7	1.18(1)
C4–O4	1.13(1)	C8–O8	1 12(1)

Bond angles

Fe1–C1–Fe2	82.8(3)	Fe3–C5–Fe4	82.5(3)
Fe1–C3–Fe2	81.4(3)	Fe3–C7–Fe4	82.3(4)
Fe1–C1–N1	135.8(7)	Fe3–C5–N2	135.2(7)
Fe1–C3–O3	141.3(9)	Fe3–C7–O7	139.8(9)
Fe1–C2–O2	175.9(8)	Fe3–C6–O6	176 9(9)
Fe2–C1–N1	141.4(8)	Fe4–C5–N2	142.3(8)
Fe2–C3–O3	137.2(9)	Fe4–C7–O7	137.8(9)
Fe2–C4–O4	179(1)	Fe4–C8–O8	178.8(8)
C1–N1–C51	126.0(8)	C5–N2–C52	125.8(8)
C1–N1–Zn	126 8(7)	C5–N2–Zn	126.1(7)
N1–Zn–N2	82.4(3)	Cl1–Zn–Cl2	113.7(1)
N1–Zn–Cl1	109.1(2)	N2–Zn–Cl1	111.0(2)
N1–Zn–Cl2	118.3(2)	N2–Zn–Cl2	118.5(2)

Best planes

I: Fe1, Fe2, C1	II: Fe1, Fe2, C3	III: Fe3, Fe4, C5	IV: Fe3, Fe4, C7
V: Cl1, Zn, Cl2	VI· N1, Zn, N2	VII: C51–C56, N1, N2	

Interplanar angles

I/II	0.9(5)	III/IV	15.5(9)	V/VI	67.3(2)
I/VI	27.5(2)	III/VI	31.2(2)	VI/VII	161.4(2)

Dihedral angles

Fe1–C1–N1–Zn	−22(1)	N1–C51–C52–N2	2(1)
Fe2–C1–N1–C51	−20(1)	C1–N1–C51–C56	−29(1)
Fe3–C5–N2–Zn	22(1)	C5–N2–C52–C53	26(1)
Fe4–C5–N2–C52	21(1)		

[a]E.s.d.s are given in parentheses. [b]The labelling of the hydrogen atoms follows that of the carbon atoms to which they are attached. C i00, Cl i1, Cl i2, H i01, H i02 ($i = 1, 2$) define the two dichloromethane solvent molecules. [c]The Roman numerals designate the following positions of equivalent symmetry: I: $-x$, $-y$, $-z$; II $x-1$, $y-1$, z; III: x, $y-1$, z; IV· $x+1$, y, z No e.s d.s are given for contact distances with generated hydrogen atoms. [d]Average.

Proton and ^{13}C NMR spectra were recorded on a Bruker AM 250 and 270 and are summarized in Tables 2 and 3. Electrolytic conductance measurements were carried out using a Metrohm conductometer E518 and an EA 608-c cell calibrated with a 0.1 M aqueous solution of KBr. C, H, N and metal analyses were obtained with a Heraeus CHN-Rapid-Elementanalysator and a Philips SP 9 AAS. Melting points were taken on a Gallenkamp melting point apparatus and are uncorrected. FAB mass spectra were obtained with a CH5-DF Varian MAT (Bremen), Pyr-EI mass spectra with a MAT 711 Varian instrument. [FeCp(CO)$_2$]$_2$ [34, 35] and PdCl$_2$(NCPh)$_2$ [35] were prepared by standard literature methods, 1,2-diisocyanobenzene (1a) as described previously [18].

Analytical data and some physical properties of the new compounds are given in Table 5. The amount of solvent of crystallization retained in the samples has been determined from the respective integrated intensities in the ^{1}H NMR spectra.

(μ_4-1,2-Diisocyanobenzene)bis(tricarbonyldicyclopentadienyldiiron) (2)

A solution of 4.00 g (11.30 mmol) of [FeCp(CO)$_2$]$_2$ in 350 ml of acetonitrile was placed in a photoreactor, cooled to -20 °C and irradiated for 12 h during which time 260 ml of CO evolved, and the reaction mixture changed colour from red to dark green [36]. At -20 °C, 0.85 g (6.64 mmol) of 1,2-diisocyanobenzene was added with stirring, and the stirring was continued for 3 h at room temperature. The solvent was removed and the brown residue extracted with 20 ml of CH$_2$Cl$_2$. The solution was then chromatographed on a water-cooled Florisil column (particle size: 0.075–0.150 mm; column dimensions: 4 cm×30 cm) made up in petrolether. Elution with petrolether/ether (3.5:1) removed some [FeCp(CO)$_2$]$_2$; further development of the column with a 1.5:1 up to 1:1 mixture of the same solvents then gave a violet and a green band the latter of which contained [Fe$_2$Cp$_2$(CO)$_3$NCMe]. The violet fraction was collected and reduced in volume until the product began to separate. Crystallization was completed by the addition of 20 ml of ether followed by 50 ml of petrolether and cooling to -18 °C to result in 1.13 g (26%) of 2 as dark red to violet needles.

MS (EI, 80 eV), m/z (rel. int. (%)): 780 (0.4), (M^+); 724 (0.6), ($M^+ - 2CO$); 546 (1), ($M^+ - FeCp - 4CO$); 519 (0.7), ($M^+ - FeCp - 5CO$), 491 (1.5), ($M^+ - FeCp - 6CO$), 186 (100), (FeCp$_2^+$).

TABLE 5. Analytical and other data

Complex	Molecular weight (g/mol)	Conductivity (S cm/mol)^a	Melting point (°C)		Analyses (%)					
					C	H	N	Fe	Other	
2	C$_{34}$H$_{24}$Fe$_4$N$_2$O$_6$ + $\frac{1}{2}$C$_4$H$_{10}$O	3 0	123–125	(found)	52.51	3 73	3.46			
	817 02			(calc.)	52.92	3.58	3.43			
3	C$_{34}$H$_{26}$B$_2$F$_8$Fe$_4$N$_2$O$_6$	156	210	(found)	42.04	3 38	2.98			
	955.58			(calc)	42.74	2.74	2.93			
4	C$_{35}$H$_{27}$BF$_4$Fe$_4$N$_2$O$_6$ + $\frac{1}{2}$CH$_2$Cl$_2$	167	165–168	(found)	46.16	3 80	3 22			
	924 26			(calc)	46 13	3 05	3 03			
5	C$_{36}$H$_{29}$BF$_4$Fe$_4$N$_2$O$_6$ + 1 5CH$_2$Cl$_2$	197	176–178	(found)	43 10	3 81	2.86			
	1023.17			(calc.)	44 02	3 03	2 74			
6	C$_{27}$H$_{19}$Fe$_3$IN$_2$O$_4$ + $\frac{1}{3}$CH$_2$Cl$_2$		176 (dec)	(found)	43 66	2.87	3 72	22 59		
	758.21			(calc)	43.30	2 57	3.69	22.09		
7a	C$_{34}$H$_{24}$Cl$_2$Fe$_5$N$_2$O$_6$ + 1 5CH$_2$Cl$_2$		64–66 (dec.)	(found)	41 34	3.07	2.75	26 78		
	1034.08			(calc)	41 23	2.63	2 71	27.00		
7b	C$_{34}$H$_{24}$Cl$_2$Fe$_4$N$_2$O$_6$Pd + $\frac{1}{2}$CH$_2$Cl$_2$		91–93 (dec)	(found)	41.02	2 68	2.95			
	999 73			(calc)	41 45	2 52	2 80			
7c	C$_{34}$H$_{24}$Cl$_2$Fe$_4$N$_2$O$_6$Zn + 2CH$_2$Cl$_2$		65–67 (dec)	(found)	39 65	2.83	2.59			
	1086.10			(calc.)	39 81	2 60	2.58			
7d^b	C$_{34}$H$_{24}$Fe$_4$I$_2$N$_2$O$_6$Zn + $\frac{1}{2}$CH$_2$Cl$_2$	3 5	77–79 (dec.)	(found)	36 29	2.38	2.44	20 27	Zn	5.86
	1141 60			(calc)	36.30	2.21	2.45	19 57		5 73
7e	C$_{34}$H$_{24}$CdFe$_4$I$_2$N$_2$O$_6$		72–75 (dec.)	(found)	35 22	2 33	2.40		Cd	9.49
	1146 16			(calc)	35.63	2 11	2.44			9.81

$^a c$ 2.0×10^{-4} M solutions in acetone ^{b} I (%): found 23 20, calc 22.23

Protonation studies and preparation of 3

To a solution of 0.26 g (0.33 mmol) of **2** in 20 ml of CH$_2$Cl$_2$ was added HBF$_4$ in ether (54%, 0.18 ml, 1.32 mmol) whereupon the solution turned light red and a microcrystalline solid began to precipitate. The precipitate was collected on a frit, thoroughly washed with ether and dried *in vacuo*. The filtrate was concentrated and layered with ether to give a second crop of red crystals. Total yield 0.29 g (91%).

In order to achieve monoprotonation 0.11 g (0.14 mmol) of **2** in 20 ml of CH$_2$Cl$_2$ was reacted with 0.019 ml (0.14 mmol) of a 54% etheral solution of HBF$_4$. No change in colour was observed. After 2 h, the solution was concentrated to about half of the original volume, and diethyl ether (5 ml) was slowly added. The red precipitate turned out to be the diprotonated species **3** while the starting complex **2** was identified as a main constituent of the filtrate.

MS (pos-FAB), m/z (rel. int. (%)): 781 (1), (M^+); 631 (3.3), $(M^+ - FeCp - CO)$; 547 (6), $(M^+ - FeCp - 4CO)$; 491 (3), $(M^+ - FeCp - 6CO)$; 454 (4.1), $(M^+ - 2FeCp - 3CO)$; 426 (7), $(M^+ - 2FeCp - 4CO)$; 398 (11.8), $(M^+ - 2FeCp - 5CO)$; 370 (9.6), $(M^+ - 2FeCp - 6CO)$.

Alkylation studies and preparations of 4 and 5

0.02 g (0.14 mmol) of acid-free trimethyloxonium tetrafluoroborate was added to 0.11 g (0.14 mmol) of **2** in 20 ml of dichloromethane, and the mixture was stirred for 3 h. The volume of the solution was then reduced to *c*. 5 ml whereupon a light red material was deposited; this was washed with ether and dried *in vacuo*. Layering of the filtrate with ether gave a second fraction of red powder which was combined with the first fraction and recrystallized from CH$_2$Cl$_2$/ether or THF/ether, respectively. Yield 0.11 g (88%).

MS (pos-FAB), m/z (rel. int. (%)): 795 (4.8), (M^+); 739 (2.1), $(M^+ - 2CO)$; 619 (37), $(M^+ - FeCp - 2CO)$; 563 (9), $(M^+ - FeCp - 4CO)$; 506 (31), $(M^+ - FeCp - 6CO)$; 441 (12.7), $(M^+ - 2FeCp - 4CO)$; 385 (23), $(M^+ - 2FeCp - 6CO)$; 320 (15), $(M^+ - 2FeCp - Cp - 6CO)$.

Essentially the same results have been obtained with a twofold excess of [OMe$_3$]BF$_4$.

The same procedure was used to synthesize the ethyl derivative **5**. Yield 85%.

Oxidation with iodine
{FeCp(I)(CO)}CNC$_6$H$_4$NC{Fe$_2$Cp$_2$(CO)$_3$} (6)

0.40 g (0.51 mmol) of **2** and 0.13 g (0.51 mmol) of elemental iodine were refluxed in chloroform (30 ml) for 1 h. The solvent was evaporated under vacuum and the red–brown residue that resulted was chromatographed on Florisil (1.5 cm × 15 cm column) with ether/petrolether (1:1) as eluent. A green band of the cleavage product FeCp(I)(CO)$_2$, and a red one containing some [FeCp(CO)$_2$]$_2$ were eluted first. THF then removed crude **6** which was recrystallized from CH$_2$Cl$_2$/ether to give 0.25 g (67%) dark red crystals.

Dichloro{(μ$_5$-diisocyanobenzene)bis(tricarbonyldicyclopentadienyldiiron)}iron(II) (7a)

0.30 g (0.38 mmol) of **2** and 0.24 g (1.90 mmol) of FeCl$_2$ were dissolved in 30 ml of CH$_2$Cl$_2$ and stirred vigorously for 12 h. After that period, the cherry-red solution was filtered and concentrated to about 10 ml, and n-hexane (5 ml) was added. Cooling of this solution to −18 °C resulted in light red microcrystals of **7a** (0.32 g, 92%) which decompose rapidly in solution at 25 °C.

Dichloro{(μ$_5$-diisocyanobenzene)bis(tricarbonyldicyclopentadienyldiiron)}palladium(II) (7b)

0.26 g (0.33 mmol) of **2** and 0.13 g (0.33 mmol) of PdCl$_2$(NCPh)$_2$ were placed in 25 ml of CH$_2$Cl$_2$ and allowed to react for 3 h during which time the product precipitated as dark red microcrystals. The crystals were filtered off, washed with ether and dried *in vacuo* to give 0.25 g (78%) of **7b**. Complex **7b** is practically insoluble in most organic solvents.

Dichloro{(μ$_5$-diisocyanobenzene)bis(tricarbonyldicyclopentadienyldiiron)}zinc(II) (7c)

0.25 ml of a 2.2 M solution of ZnCl$_2$-diethyletherate (0.55 mmol) in dichloromethane was added to 0.37 g (0.47 mmol) of **2** in 40 ml of CH$_2$Cl$_2$. After standing for 2 h, the reaction mixture was reduced in volume and layered with petrolether which afforded 0.40 g (92%) of dark red needles.

Diiodo{(μ$_5$-diisocyanobenzene)bis(tricarbonyldicyclopentadienyldiiron)}zinc(II) (7d)

The heterogeneous mixture of 0.40 g (0.51 mmol) of **2**, dissolved in 30 ml of CH$_2$Cl$_2$, and 0.33 g (1.00 mmol) of solid ZnI$_2$ was stirred at room temperature for 3 h. By then the suspension had turned cherry-red and was filtered to remove the unreacted ZnI$_2$. The filtrate was concentrated to 15 ml, layered with 5 ml of petrolether and allowed to stand at 6 °C which resulted in dark red crystals. Yield 0.51 g (90%).

Diiodo{(μ$_5$-diisocyanobenzene)bis(tricarbonyldicyclopentadienyldiiron)}cadmium(II) (7e)

0.42 g (1.20 mmol) of CdI$_2$ were suspended in a solution of 0.30 g (0.38 mmol) of **2** in 30 ml of CH$_2$Cl$_2$, and the mixture was stirred for 6 h. After filtration, the cherry-red solution was reduced in volume to 10 ml, layered with 5 ml of n-hexane and cooled to −18 °C. Light red microcrystals (0.42 g, 95%) started growing overnight.

TABLE 6 Fractional atomic coordinates and thermal parameters of the non-hydrogen atoms

Atom	x/a	y/b	z/c	U_{eq}[a]
Fe1	0.1143(1)	0 63591	0 34530(6)	2 85(5)
Fe2	0.3135(1)	0.7096(1)	0.39521(6)	2 86(5)
Fe3	0.1105(1)	1.2022(1)	0 06909(6)	2 70(5)
Fe4	0.3159(1)	1 2883(1)	0.10958(6)	2.93(5)
Zn	0.0338(1)	0.94557(9)	0.22066(5)	3 04(4)
Cl1	−0.2200(3)	0.9881(2)	0 2461(1)	4 7(1)
Cl2	0.0960(3)	0 8209(2)	0.1515(1)	4.8(1)
N1	0.1385(8)	0.9036(6)	0 3045(3)	2.7(3)
N2	0 1418(8)	0.1041(6)	0 2058(3)	2 7(3)
O2	0.3213(9)	0 5610(7)	0.2379(4)	6.2(4)
O3	0.2769(8)	0 4475(6)	0.4349(3)	4 8(3)
O4	0.892(1)	0.2422(7)	0 4929(4)	6.2(4)
O6	0.3109(9)	−0 0004(7)	0.0228(4)	5 8(3)
O7	0 7303(8)	0.6122(6)	0.0230(3)	5.0(3)
O8	0 119(1)	0.5039(7)	0.1435(4)	6 5(4)
C1	0.1758(9)	0 7956(8)	0 3366(4)	2.7(3)
C2	0.241(1)	0 5945(8)	0.2786(5)	3.8(4)
C3	0 248(1)	0.5462(9)	0 4049(4)	3.5(4)
C4	0.189(1)	0 7400(9)	0 4633(5)	3.8(4)
C5	0.1783(9)	0 1723(7)	0.1520(4)	2 4(3)
C6	0.234(1)	0.0781(9)	0.0424(5)	3.8(4)
C7	0.245(1)	0 3219(9)	0 0271(5)	3 7(4)
C8	0 195(1)	0 4198(9)	0.1310(5)	4.0(4)
C11	0 945(1)	0.544(1)	0.3237(6)	5 4(5)
C12	0.954(1)	0.509(1)	0 3886(6)	5.6(5)
C13	0.919(1)	0 617(1)	0 4147(5)	5.8(5)
C14	0.887(1)	0.716(1)	0.3645(7)	5.6(5)
C15	0.903(1)	0.669(1)	0 3091(5)	5.3(5)
C21	0.520(2)	0 678(3)	0 4325(9)	11(1)
C22	0.490(2)	0.799(2)	0.408(1)	10(1)
C23	0 490(2)	0.813(2)	0.347(1)	9 3(8)
C24	0.516(2)	0.702(3)	0.3311(9)	12(1)
C25	0 535(2)	0.616(1)	0.386(2)	12(1)
C31	0 900(1)	0.131(1)	0.0820(5)	4 7(4)
C32	0.938(1)	0 181(1)	0 0166(5)	5.3(5)
C33	0.945(1)	0.306(1)	0 0108(5)	5.1(5)
C34	0.913(1)	0.338(1)	0 0719(6)	5.3(5)
C35	0.884(1)	0 227(1)	0 1153(5)	5.0(5)
C41	0.494(1)	0.188(1)	0.1605(6)	6 0(5)
C42	0.497(1)	0 313(1)	0 1549(8)	7 5(7)
C43	0.524(1)	0.362(1)	0.088(1)	8.2(8)
C44	0 537(1)	0.267(2)	0.0558(6)	7.7(7)
C45	0.516(1)	0.160(1)	0 1010(8)	7.4(7)
C51	0.170(1)	0 0185(8)	0.3173(4)	3.1(3)
C52	0 175(1)	0.1203(8)	0 2666(4)	2.9(3)
C53	0.197(1)	0 2343(9)	0 2787(5)	4 8(4)
C54	0.220(1)	0 2457(9)	0.3391(5)	5.0(4)
C55	0 211(1)	0.1476(9)	0 3892(5)	4 9(4)
C56	0.184(1)	0.0351(9)	0.3788(4)	4.1(4)
Cl11	0.7235(5)	0.5863(4)	0.1836(2)	9 4(2)
Cl12	0.5152(5)	0.7968(4)	0.1365(2)	11.2(2)
C100	0 703(2)	0 744(2)	0.1463(6)	9.5(8)
Cl21	0.708(1)	0.0443(9)	0 4369(4)	28.5(7)
Cl22	0.644(1)	0 2774(9)	0.3609(7)	36(1)
C200	0.766(2)	0.155(2)	0.371(1)	14(1)

[a]$U_{eq}=\frac{1}{3}\Sigma_i\Sigma_j a^*_i a^*_j a_i a_j$.

X-ray crystal structure determination

Single crystals of **7c** ($C_{34}H_{24}Cl_2Fe_4N_2O_6Zn + 2CH_2Cl_2$ $M = 1086.10$) were grown from a saturated solution in CH_2Cl_2/petrolether by lowering the temperature from $+21$ to $+15$ °C within 12 h. A crystal of size $0.10 \times 0.14 \times 0.80$ mm was mounted under argon in a glass capillary. All crystallographic data were collected at 293 K on a STOE four circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). Unit cell parameters (triclinic, $P\bar{1}$ (No. 2), $a = 8.882(2)$, $b = 11.084(2)$, $c = 21.444(4)$ Å, $\alpha = 78.1(1)$, $\beta = 81.4(2)$, $\gamma = 81.7(2)°$, $U = 2028.13$ Å^3, $Z = 2$, $D_c = 1.735$ g cm^{-3}) were obtained by a least-squares refinement of the angular settings from 25 reflections, well distributed in reciprocal space and lying in a 2θ range of 20–30°. A total of 6379 reflections was measured (ω-scan mode, $4 \leqslant 2\theta \leqslant 45°$) of which 4132 were considered 'observed' ($I \geqslant 2\sigma(I)$). They were corrected for Lorentz and polarization effects as well as for absorption (μ(Mo $K\alpha) = 22.0$ cm^{-1}). The structure was solved by employing a combination of direct methods and difference Fourier techniques with scattering factors for neutral atoms taken from the literature [37]. All calculations were carried out on a VAX computer using the programs SHELXS-86 [38], XTAL 2.2 [39], DIFABS [40] and ORTEP [41]. After all of the non-hydrogen atoms were located and refined (Table 6), the hydrogen atoms were generated in positions of idealized geometry. In the final cycles of refinement, anisotropic thermal parameters for the non-hydrogen atoms were included (496 parameters altogether), while the coordinates and thermal parameters of the hydrogen atoms were kept at fixed values. The full-matrix least-squares refinements were based on F, and the function minimized was $\Sigma w(|F_o| - |F_c|)^2$. Refinement was terminated when the maximum shift in any parameter was $< 10^{-4} \sigma$. The final R ($= \Sigma||F_o| - |F_c||/\Sigma|F_o|$) was 0.051 and R_w ($= [\Sigma(w||F_o| - |F_c||^2)/\Sigma(w|F_o|^2)]^{1/2}$) was 0.056, where $w = \{\sigma(F_o)\}^{-2}$.

Supplementary material

Tables of anisotropic thermal parameters for the non-hydrogen atoms (Table 7) and hydrogen positional and thermal parameters (Table 8), and listings of observed and calculated structure factors for all observed reflections are available from the authors on request.

Acknowledgements

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