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Reaction patterns of 'tetraferrio-azaallenium', $[(OC)_3Cp_2Fe_2(\mu_4-C=N=C)Fe_2Cp_2(CO)_3]^+$, and its 'activated cyanide'-precursor (µ-phthalimidocarbyne)tricarbonyldicyclopentadienyldiiron(1 +)^{*}

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Abstract

(u-Phthalimidocarbyne)tricarbonyldicyclopentadienyldiiron(1 +) (2) which, due to the facile cleavage with cis-[Fe₂Cp₂(CN)(u- $(CO)_2CO]^-$ (1) of its μ -CN bond to give 'tetraferrio-azaallenium' $[(OC)_3Cp_2Fe_2(\mu_4-C=N=C)Fe_2Cp_2(CO)_3]^+$ (3), has been termed 'activated cyanide' reacts with pyrrolidine with ring opening to give the µ-acylisocyanide complex 5 carrying a further amido function in the o-position. Butyllithium gives rise to only traces of the corresponding mono-deacylation product 6 while the main product is 3. Formation of complex 3 which is presumed to occur via partial bis-deacylation of 2 to give 1 and subsequent recombination with loss of phthalimide also dominates the reactions of 2 with CN^- and $[W(CN)(CO)_5]^-$. Here, however, the nucleophile also attacks the μ -carbyne carbon atom to give moderate yields of the desired μ -cyanoalkyliden complexes 7 and 10, the latter with $[W]CN \leftrightarrow [W]NC$ isomerization and C-C bond formation. With $[Cr(CN)(CO)_s]^-$, in contrast, substitution of a terminal CO ligand occurs with formation of the cyano-bridged trinuclear complex 9. The structures of complexes 7, 9 and 10 have been elucidated by X-ray analysis. Action upon 'tetraferrio-azaallenium' 3 of the primary amines $H_2NCH_2CH_2R$ (R = Me, OMe, Ph) gives rise in low yields to the respective terminal isocyanides in compounds 11-13. Here as in the reaction with NaNH₂ to give 14, a terminal carbonyl ligand is converted into an isocyanide or, respectively, cyano ligand by an exchange of oxygen for NR (N⁻). A second though less efficient approach to 14 is CO substitution in 3 by NaCN. Disubstitution of 3 to give 15 is observed with trimethylphosphite. In the reactions of 3 with diamines (H₂NCH₂CH₂NH₂, H₂NCH₂CH₂CH₂CH₂CH₂NH₂), on the other hand, cluster fragmentation occurs with formation of the mononuclear complexes 16 and 17 containing cyclic diaminocarbene ligands. A cyclic µ-aminocarbyne diiron complex 18 is obtained in traces from 3 and pyrrolidine. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Iron complexes; Imidocarbyne bridged complexes; Polynuclear complexes

1. Introduction

Our continuous interest in the development of a cyano complex based organometallic chemistry had

prompted us to search for simple cyano clusters which, in addition to the terminal coordination mode, would offer μ -C,C bridging positions to the cyano ligand or its eventual reaction products with very different implications for the stereochemistries and reactivities of the respective groups [1]. The synthesis of *cis*-[Fe₂Cp₂-(CN)(μ -CO)₂CO]⁻ (1) [2], the elucidation of its dynamics and the results of its protonation [3], alkylation, acylation and iminoacylation studies [4] have met these expectations at the same time considerably extending this type of chemistry.

^{*} Chemistry of Hydrogen Isocyanide, Part 14. For Part 13 see Ref. [6].

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A wholly new dimension reaching far beyond cyanide acylation arose, however, on the attempt of diacylation of 1 with phthaloyl dichloride. Here, instead of the expected product 2 we got a unique tetranuclear cation, the tetrametallated azaallenium species 3, which in spite of the very mild conditions prevailing during the reaction must have formed by an unprecedented aprotic cleavage of the CN triple bond and by fixation of the formally resulting μ -carbido diiron fragment to a second cyano diiron complex anion [5].



Concerning the mechanism, we had intuitively favoured 2 as the reaction intermediate from the beginning though at that time diacylation of the µ-CN ligand had not been achieved in any case. Recently, however, we succeeded in the preparation and structural characterization of 2 and a series of related compounds with N,N-diacylated cyano bridges all of which showed dramatically elongated µ-C-N bonds of > 1.30 Å [6]. Chemical proof that 2 and its congeners were in fact the long sought after 'activated cyanide'-intermediates in the formation of tetraferrio-azaallenium (3) has been furnished by their 1:1 reactions with the cyano diiron anion 1 rendering 3 in practically quantitative yields. In order to obtain this result, the nucleophile, i.e. the nitrogen end of the terminal cvano ligand in 1, must have attacked the carbyne carbon of 2 to give a μ -alkylidene intermediate A $(Nu = N \equiv C - Fe_2Cp_2(CO)_3)$ which subsequently underwent some $(CN)_{terminal} \rightarrow (CN)_{bridge}$ rearrangement with loss of phthalimide. From the reaction with 1 of the glutarimido analogue of 2, however, only a minor amount of 3 could be isolated together with traces of a byproduct of the form 4 revealing a competing situation in 'activated cyanides' between the carbyne carbon atom (C¹) and a second electrophilic centre located on the acyl groups (C^3) , which is reminiscent of another type of 'activated (iso)cyanide', viz. $Cr(CO)_5C^1 \equiv N - C^3Cl_3$ [7].

In this paper we report on the reactions of 2 and 3 with nucleophiles other than 1 which have been studied with the intention of gaining more insight in the chemistry of these novel, obviously highly electrophilic species in general. Particular interest was shown in the possibility of using 2 (and perhaps also 3) as sources of C_1 fragments for the construction of new metallated CNC (or CCN) moieties with various other cyanides (Scheme 1).



Scheme 1. [Fe] = $Fe(\eta$ -Cp)CO; [Fe₂] = $Fe_2(\eta$ -Cp)₂(CO)₃.

2. Addition of nucleophiles to the μ -phthalimidocarbyne diiron complex 2

2.1. Reactions with pyrrolidine and butyllithium

Formal transfer of $[Fe_2]C^{2+}$ ($[Fe_2] = Fe_2(\eta-Cp)_2$ -(CO)₃) onto secondary amines NHRR' promised a new approach to aminocarbyne bridged diiron comof the formula $[Fe_2Cp_2(CO)_2(\mu-CO)($ plexes C=NRR']⁺. A wide range of alicyclic aminocarbyne complexes of this type have been prepared by Manning and coworkers [8] through alkylation of the respective alkylisocyanide starting materials. A cyclic analogue $[Fe_2Cp_2(CO)_2(\mu-CO)(\mu-C=N(CH_2)_3CH_2)]^+$ (cf. Section 3.3), has been synthesized in our group by reacting Fe₂Cp₂(CO)₄ or [Fe₂Cp₂(NCMe)(CO)₃], respectively, with 4-chlorobutyl isocyanide [9]. The product obtained quantitatively from the reaction of 2 with pyrrolidine, however, is clearly not of this type. The characteristic vC=N < band in the IR around 1590 ± 15 cm⁻¹ is missing while the absorptions present at 1690 m $[v(CO)_{acvl}]$ and 1630 versus [v(C=N)]are indicative of the µ-acylisocyanide grouping. Thus, unlike 1, which in the case of the glutarimido derivative of 2 produced only traces of the $bis(\mu-acyliso$ cyanide) 4 while no byproducts have been observed in the reaction with 2 (see above), pyrrolidine attacks exclusively at the C³ position causing partial deacylation of the 'activated cyanide' with ring opening and formation of the 'mixed amide' 5. According to an IR spectrum the same reaction pattern applies with npropylamine; therefore no effort was made to purify the crude product.

One plausible product from the action upon 2 of butyllithium could have been A (Nu = Buⁿ) which, due to the preformed phthalimide leaving group, was expected to give the secondary reactions of a μ -alkylidyne species [10]. A promising model for the formation of new C–C bonds with carbanions exists in Busetto and co-workers [Fe₂Cp₂(CO)₃(μ -CSMe)]-CF₃SO₃ [11]. The actual findings, however, were even more disappointing than those with pyrrolidine. In addition to some unreacted starting material only minor amounts of a monodeacylation product, $Fe_2Cp_2(CO)_3\{\mu$ -CNC(O)C₆H₄-o-C(O)Buⁿ\} (6), could be isolated.

What significantly prevails in this reaction (and in most of those to be reported in the following) is the formation of the tetraferrio-azaallenium 3, the obvious thermodynamic sink in the system. As outlined in Eq. (1), for 3 to form, total, i.e. two-fold deacylation of the 'activated cyanide' must occur to afford free cyanodiiron complex anions which then recombine with remaining phthalimidocarbyne diiron complex cations in the familiar way [6]. It should be noted that none of the side products C have been observed in any case.

$2 + Nu \rightarrow Fe_2Cp_2(CO)_3\{\mu-CNC(O)C_6H_4-o-C(O)Nu\}$



2.2. Reactions with cyanide and cyanometallates

The main product of the reaction of cyanide applied as NaCN with 2 (as PF_6 salt) in 1,2-dimethoxyethane was again tetraferrio-azaallenium 3; neither an intermediate **B** (Nu = CN) nor the expected byproduct **C** (Nu = CN) have been identified in the workup procedure. Instead, a neutral complex (7) could be separated by fractional crystallization showing all the analytical, spectroscopic (IR, MS) and structural requirements (see Sections 4 and 2.3) for the desired primary adduct A (Nu = CN). Interestingly, there were no indications of a spontaneous release of the phthalimide leaving group to end up with a cationic μ -cvanocarbyne diiron complex, nor was there any evidence of a µ-dicyanocarbene product. The latter has been obtained by Busetto and co-workers [12] from an ylid-like storage form **D** which dissociates much easier than A as no charge separation is required.

By employing the cyanometallates $[M(CN)(CO)_5]^-$ (M = Cr, W) we once again borrowed from Busetto's fine chemistry which by reaction of the carbocationic **D** with (a) CN⁻ followed by $W(CO)_5$ thf or (b) $[W(CN)(CO)_5]^-$ had brought about the two isomers **E** (Scheme 2).

As part of a more general program which focuses on the question of metal stabilization of the 'nonexisting' CNC in forms such as **3** ('permetallated azaallenium') or **8** ('permetallated methylisocyanide' [13]), we have also become interested in metallacumulenes of type **F** for which the chemistry of this paragraph might open a possible route.



Scheme 2. $[Fe_2] = Fe_2(\eta - Cp)_2(CO)_3$.

Again, we have to state that with both reagents addition to the acyl function in 2 predominates with the familiar consequence of 3 being the main product. In the case of $[Cr(CN)(CO)_5]^-$, the expected side product $(OC)_5 CrCNC(O)C_6H_4 - o - C(O)NCCr(CO)_5$ has been identified. However, there were accompanying products (9, 10), both of which gave us a surprise. Though analyzing as simple neutral 1:1 adducts, major inconsistencies in the v(CN) and v(CO) regions of the IR and particularly, the ¹H NMR made us envisage rather different structures for 9 and 10. In compound 9 it was the nonequivalence of the two iron centres as indicated by two Cp signals of equal intensity (Section 4) which put us on the track of a possible CO substitution by [Cr(CN)(CO)₅]⁻, a proposal later confirmed by an X-ray structure analysis (Section 2.3). What made us hesitate to formulate 10 as the hoped-for μ_3 -isocyanocarbene species A $(Nu = NCW(CO)_5)$, on the other hand, was the unusually high IR frequency of 2175 cm⁻¹ of the presumed tungsten-coordinate isocyanide. Here, Busetto's isomers with v(CN) = 2198 for E(a) versus 2125 cm⁻¹ for E(b) turned out to be ideal for comparison. Verification of the obvious conclusion that a NCW/CNW-isomerization with CC-bond formation must have occurred during or after the nucleophilic addition to the carbyne carbon of 2 again is provided by structure determination (see below). Notice that in the very similar preparation of E(b) no such isomerization was observed (Scheme 3).

2.3. X-ray structures of 7, 9 and 10

The configuration of complexes 7 and 10 is *cis* with the two Cp ligands sticking out on one side of the best plane through the Fe₂(μ -C)₂ rhomboid, and the two terminal CO groups on the other (Figs. 1 and 2). Identical values (163(1)°) are found for the interplanar angles Fe1Fe2(μ -C)/Fe1Fe2(μ -C'), which describe the fold of the central four-membered ring along the Fe1···Fe2 axis.

The μ -alkylidene carbon is quasi-tetrahedral with C–N and C–C single bonds (Tables 1 and 3) and N–(μ -C)–C angles between the freely adjusting phthalimido and cyano or, respectively, CNW(CO)₅ substituents of 105(1) and 104(2)°, i.e. close to the ideal



Scheme 3. [Fe] = $Fe(\eta$ -Cp)CO.

value. The planar phthalimido group is practically perpendicular to the N,(μ -C),C plane which in turn is perpendicular to Fe1Fe2(μ -C_{carbene}). The remaining bonding parameters are all in the usual range.

Some effort has been made to furnish unequivocal proof of the nitrile structure of complex 10. The usual strategy, viz. comparison of the effects on the temperature factors of several cycles of refinement for the two atomic arrangements in question $[Fe_2]C-N\equiv C-W$ or $[Fe_2]C-C\equiv N-W$, has also been successful in the present case. Fig. 3 depicts the thermal ellipsoids resulting from



Fig. 1. Molecular structure of complex 7.



Fig. 2. Molecular structure of complex 10.

two calculations with exchanged C and N scattering factors which are clearly in favour of $[Fe_2]C-C=N-W$; for the corresponding U₁₁ values (see caption).



Fig. 3. ORTEP drawing of the central linkage after two cycles of refinement with (a) $[Fe_2]C-C-N-[W]$ (U₁₁(C) 4.48(4), U₁₁(N) 4.35(5)) and (b) $[Fe_2]C-N-C-[W]$ (U₁₁(N) 1.66(8), U₁₁(C) 7.86(5)) atomic sequences.

Table 1

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Selected bond distances (Å) and bond angles (°), best planes and interplanar angles (°) of 7 a

Bond distances (A)			
Fe1–Fe2	2.513(3)	Fe1–C3	1.87(2)
Fe1–C4	1.97(2)	Fe1–C1	1.75(2)
Fe2–C2	1.75(2)	Fe2–C3	1.92(2)
Fe2–C4	1.98(2)		
Fel-C(Cp) ^b	2.12(2)	Fe2–C(Cp) ^b	2.12(2)
O1C1	1.14(3)	O2–C2	1.13(3)
O3–C3	1.21(2)		
N1-C4	1.45(2)		
N1-C11	1.44(2)	N1-C12	1.41(2)
N2-C5	1.12(3)	C4–C5	1.51(3)
O11-C11	1.16(2)	O12–C12	1.24(2)
C11–C13	1.49(3)	C12–C18	1.42(2)
C13–C14	1.42(3)	C13–C18	1.39(2)
C14–C15	1.44(3)	C15–C16	1.40(3)
C16–C17	1.41(3)	C17–C18	1.39(3)
Bond angles (°)			
FeI-Fe2-C2	99.1(6)	Fel-Fe2-C3	47.6(6)
Fel-Fe2-C4	50.3(5)		
Fe2–Fe1–C1	98.7(7)	Fe2–Fe1–C3	49.4(6)
Fe2–Fe1–C4	50.6(6)		
Fe1–C3–Fe2	83.0(8)	Fel-C4-Fe2	79.1(7)
Fel-Cl-Ol	178(2)	Fel-C3-O3	141(2)
Fel-C4-N1	124(1)	Fel-C4-C5	112(1)
Fe2–C2–O2	177(2)	Fe2–C3–O3	136(2)
Fe2–C4–N1	123(1)	Fe2-C4-C5	113(1)
C1–Fe1–C3	87(1)	C1–Fe1–C4	90.5(8)
C2–Fe2–C3	86.6(9)	C2–Fe2–C4	92.5(8)
C3–Fe1–C4	98.4(8)	C3–Fe2–C4	96.4(8)
C4-N1-C11	124(1)	C4-N1-C12	125(1)
C4-C5-N2	178(2)		
N1-C4-C5	105(1)		
N1-C11-O11	125(2)	N1-C12-O12	121(2)
N1-C11-C13	102(1)	N1-C12-C18	109(1)
C11-N1-C12	110(1)		
O11-C11-C13	132(2)	O12-C12-C18	129(2)
C11-C13-C14	124(2)	C11-C13-C18	111(1)
C12-C18-C13	107(1)	C12-C18-C17	133(2)
C13-C14-C15	113(2)	C13-C18-C17	121(2)
C14-C13-C18	125(2)	C14-C15-C16	123(2)
C15-C16-C17	121(2)	C16-C17-C18	118(2)
Best planes			
I: Fe1, C3, Fe2	II: Fe1, C4, Fe2		III: C5, C4, N1
IV: N1, C12, C18, C13, C11	V: C13, C14, C15, C16, C17, C18		
Interplanar angles (°)			
I/II: 17(1)	II/IV: 137(1)		III/IV: 84(1)
IV/V: 0.9(5)			

^a E.s.d.s are given in parentheses, see Fig. 1 for atomic numbering.

^b Average value.

The core of complex **9**, in contrast, is configurated *trans* exhibiting an asymmetry which reflects its asymmetric substitution (Fig. 4, Table 2). Why $[Cr(CN)(CO)_5]^-$ chooses to attack at the iron atom in the second place, i.e. after having largely deacylated the 'activated cyanide' remains in the dark. Steric reasons can definitely be ruled out as is obvious from the tungsten case **10** and the quantitative reaction between **2** and $[Fe_2Cp_2(CN)-(CO)_3]^-$. Moreover, the minimal steric requirements of

 $[M(CN)(CO)_5]^-$ have impressively been demonstrated by its extensive use as a ligand in hexacoordinated supercomplexes of the type $[M'{NCM(CO)_5}_6]^{x-6}$ (M = e.g. Si(IV), Cr(III)) ('octahedro octahedra') [14].

Actually, most of the stereochemical peculiarities in 9 (as compared to, e.g. 7 and 10 or better 2 and the other 'activated cyanides' [6]) can be traced back to the presence of the electron-rich pentacarbonyl (cyano)chromate in the place of a π -acidic CO ligand.



Fig. 4. ORTEP drawing of compound 9.

The afore-mentioned asymmetry of the Fe₂(μ -C)₂ core with the unusually short Fe1–C2 bond of pronounced double bond character—the 180(1) pm correspond well with the 180.3(5) pm for the Fe=C bond in Berke's ferra-cumulene (OC)₄Fe=C=C=CC(Bu^t)₂OC(O)O [15]—finds its logical consequence in an extremely elongated C2–N2 bond of 137(1) (!) pm, which sets up a new record within the family of 'activated cyanides' [6]. The bonding which resembles that in formamides (C–N: 136 pm) is perhaps best represented by resonance formula **G**.



3. The nucleophilic reaction pattern of tetraferrio-azaallenium (3)

The agreement of the measured C=N bond lengths in 3 with those calculated by geometry optimization for the model and parent compounds $Li_2C=N=CLi_2^+$ and $H_2C=N=CH_2^+$ as well as the continual preference of the cumulene over the tautomeric bent 2-azaallylium form shows, that contrary to lone pair donor substituents (-OR, NR₂) [16], no unusual electronic effects are exerted by the organometallic substituents in tetraferrio-azaallenium ions. As calculations on azaallenium ('bisiminium') compounds in general have also established a highly electrophilic character of the carbon atoms, we expected nucleophilic attack on **3** to occur at these positions with formation of imine-type structures and the possibility of obtaining the bis(μ -methyliden)amine structures **H** (Eq. (2)), provided the C=N=C framework was sufficiently accessible in spite of its steric shielding by the substituents on iron as apparent from a space-filling model of the cation of **3** (see Fig. 1 in Ref. [5]).



3.1. Addition of primary amines. Isocyanide derivatives

Reactions between 3 and primary amines require distinctly higher temperatures (Section 4). The only products which could be isolated in low yields besides unreacted starting material were the mono-isocyanide derivatives of 3, 11-13, i.e. nucleophilic attack occurred solely at the carbon atom of a terminal CO ligand. It is very likely that steric reasons have to be put forward for this chemistry forced entirely to the periphery (see above).

Methods for the synthesis of isocyanides at metal complexes have been extensively studied in our group including the conversion of CO into CNR ligands [17–19]. The latter generally proceeds in two steps via intermediate carbamoyl (carboxamido) species which is easily dehydrated with phosgen in analogy to the preparation of isocyanides from formamides (Eq. (3)) [19].

$$[M]C \equiv O + RHN_2 \rightarrow [M]C(=O)NHR^{\top} \rightarrow [M]C \equiv NR$$
(3)

At the elevated temperatures applied in the present case, dehydration must have occurred spontaneously as no carbamoyl complexes have been detected.

Number, positions and intensities of the characteristic bands and signals in the IR and ¹H NMR spectra, respectively, are in accord with the assigned structures (Section 4). Compared with the related isocyanide complexes $[Fe_2Cp_2(CO)(CNMe)(\mu-CO)_2]$ (2138 cm⁻¹) and $[Fe_2Cp_2(CO)(CNMe)(\mu-CO)(\mu-CN(H)Me)]^+$ (2189 cm⁻¹), the $\nu(CN)$ IR frequencies of complexes 11–13 (2153 ± 5 cm⁻¹) reflect (a) the cationic overall charge which (b) is spread across four

Table 2

Selected bond distances (Å) and bond angles (°), best planes and interplanar angles (°) of 9^{a}

Bond distances (Å)			
Fe1–Fe2	2.508(3)	C3–O3	1.15(2)
Fe1-N1	1.92(1)	C4–O4	1.18(2)
Fe1–C2	1.80(1)	C6–O6	1.19(2)
Fe1–C4	1.89(1)	C9–O9	1.17(2)
Fel-C(Cp) b	2.12(2)	C13-O13	1.16(2)
Fe2–C2	1.86(1)	C11-O11	1.16(2)
Fe2–C3	1.77(1)	C12-O12	1.12(2)
Fe2–C4	1.93(2)	C14-O14	1.15(2)
Fe2–C(Cp)	2.10(2)	C15-O15	1.16(2)
Cr-C1	2.03(2)	C6-C7	1.50(2)
CrC13	1.86(2)	C7–C8	1.37(2)
Cr-C11	1.86(2)	C7-C16	1.37(2)
Cr-C12	1.92(2)	C8–C9	1.49(2)
Cr-C14	1.89(2)	C8-C19	1.44(2)
Cr-C15	1.89(2)	C16-C17	1.42(2)
N1-C1	1.18(2)	C17-C18	1.37(3)
N2-C2	1.37(1)	C18-C19	1.42(2)
N2-C6	1.45(2)		
N2-C9	1.45(2)		
Bond angles (°)			
Fe1-C2-Fe2	86.6(5)	C6-C7-C8	107(1)
Fe1–C4–Fe2	82.0(5)	C7–C8–C9	112(1)
C1CrC13	177.5(8)	C6-N2-C9	110.2(9)
C12CrC15	176.6(7)	C8-C7-C16	126(1)
C11-Cr-C14	178.3(8)	C7-C16-C17	113(2)
C2-N2-C6	125(1)	C16-C17-C18	124(2)
N2-C6-O6	125(1)		
Best planes			
I: Fe2, C2, Fe1		III: N2, C6, C9, C8, C	7
II: Fe2, C4, Fe1		IV: C7, C8, C19, C18,	C17, C16
Interplanar angles (°) I/II: 176.1(6) I/III: 150.3(4))	III/IV: 179.6(4)	

^a E.s.d.s are given in parentheses, see Fig. 4 for atomic numbering. ^b Average value. coordination centres. Due to the low solubility of the complexes no ¹³C NMR spectra could be obtained.



3.2. Cyano and phosphite derivatives of 3

Tetraferrio-azaallenium is strikingly inert. Even the small, negatively charged nucleophiles NH₂⁻ and CN⁻ do not react at ambient temperature. Heating mixtures of 3 and sodium amide suspended in dioxane for several hours to above 100°C resulted in very modest yields of the neutral cyano cluster 14. The starting complex is recovered almost quantitatively. Again the terminal carbonyl carbon atom proves to be the most reactive since it's the most easily accessible site in the molecule. A vast number of similar transformations of carbonyl to cyano ligands has been carried out by reaction in liquid ammonia [20c]. They are known to proceed via unsubstituted carbamoyl species $([M]-C(=O)HN_2)$ which subsequently are dehydrated. A major improvement was reached with the introduction of 'silazid' (NaN(SiMe₃)₂) as reagent which allowed these reactions to be conducted under aprotic (anhydrous) conditions [20a,b].

Identical conditions have been applied for the reaction of **3** with NaCN and practically identical results have been achieved (Section 4). Neither here nor in the case of NaNH₂ have we made any move to improve the yields. Yet knowing that substitutions are possible, we started to look at some more. Of the potential ligands employed, however, only $P(OMe)_3$ gave minimum amounts of a doubly phosphite-substituted derivative **15**. Two singlets in the ¹H NMR for the Cp ligands clearly indicate that the substitutions occurred at iron atoms related by a two-fold rotation axis, the only symmetry element present in **3** (see above and [5]). No reaction was observed with the phosphines PPh₃ and PBu₃ⁿ.





3.3. Nucleophilic additions with cluster fragmentation

For the reactions with diamines (1,2-diaminoethane, 1,4-diaminobutane) we chose conditions identical to those for the amine reactions (Section 2.1). In the first step the reactions appear to proceed in the same fashion forming terminal isocyanide ligands I which, however, are 'functional', i.e. carry further NH₂ groups in their side chains. Functional isocyanides of this type are unstable both in the free and coordinated state, immediately undergoing cyclization to give (carbenoid) N,N'-heterocycles. In fact, we observe species (16, 17) with this kind of ligand along with a typical degradation product, $[Fe_2Cp_2(CO)_4](Fp_2)$, yet they are mononuclear iron(II) compounds. In the end it is probably the presence of three strong electron donors in this array of four different ligands about the tetrahedral center which causes the cluster to break up into fragments.

Of five secondary amines tested for reactions with **3** only pyrrolidine gave rise, besides Fp_2 , to an identifiable product **18**. Actually, this is the first and only case in which the carbido species $[Fe_2Cp_2(CO)_3\mu-C]^{2+}$ has formally been transferred to a substrate (see Section 2.1).

4. Experimental

All operations were carried out under an atmosphere of pure argon using Schlenk-tube and vacuum techniques. The organic solvents were dried, distilled and stored under argon. IR spectra were run on Perkin–Elmer model 983 and Beckman model 4240 spectrometers. Microanalyses (C, H, N) were obtained with a Heraeus CHN-Rapid analyzer. Melting points were taken on a Gallenkamp MFB-595 apparatus and are uncorrected. Mass spectra (EI, pos-FAB) were obtained with Finnigan (Varian) MAT 711 (excitation energy 80 eV), MAT 112 S and MAT CH5-DF (neutral xenon source at 3 keV, co-solvent DMSO, matrix 3-nitrobenzyl alcohol) instruments. Proton and ¹³C NMR spectra were recorded on a Bruker AC 250 and a Bruker SY 270 spectrometer. Silica gel (100–200 μ m) from ICN and aluminium oxide (N, Akt. I) from Woelm–Pharma were used for chromatography.

Complexes **2** (as PF_6 salt) [6], **3** (as BF_4 salt) [5], $NEt_4[Cr(CN)(CO)_5]$ and $NEt_4[W(CN)(CO)_5]$ [21] were prepared according to published procedures.

4.1. Reaction of 2 with pyrrolidine 5

A suspension of 0.35 g (0.55 mmol) of $2-PF_6$ in 10 ml of THF was cooled by means of an ice-bath. To this pyrrolidine (0.11 ml, 1.11 mmol) was dropped quickly causing the suspension to clear up to a deep red solution. For the reaction to be completed the mixture was stirred for another 3 h at room temperature (r.t.). After removal of the solvent the crude product was purified by chromatography on a silica charged column $(2 \times 15 \text{ cm})$ with THF/ether (1/1) as eluent. The first red phase containing the ring-opened product was collected, reduced to about half of its volume and layered with light petroleum (40-60°C). Within 24 h the product crystallized as deep red thin rods. Yield 0.11 g (36%). M.p. 165-167°C. Anal. Calc. for $C_{26}H_{22}Fe_2N_2O_5$ (554.16 g mol⁻¹): C, 56.35; H, 4.00; N, 5.06. Found: C, 56.32; H, 4.09; N, 5.01%. IR (CH_2Cl_2, cm^{-1}) : 2001vs, 1995vs, 1957m [$\nu(CO)_{term}$]; 1794m-s [ν(μ-CO)]; 1691m,br [ν(C=O)_{acvl}]; 1630vs [ν(μ-CN)]. ¹H NMR (δ , CD₃CN): 8.25–7.40 (4H, Ph); 5.04 (s, 10H, Cp); 3.61 (t, 2H, CH₂, J_{HH} 4.48 Hz); 3.21 (t, 2H, CH₂, J_{HH} 4.48 Hz); 1.94 (m, 4H, CH₂). ¹³C{H} NMR (δ, CDCl₃): 268.8 (μ-CO); 263.4 (μ-CN); 209.8 (CO)_{term}; 155.4 (>C=N-C=O); 140.8 (>NC=O); 132.7, 131.7, 131.0, 128.5, 127.3, 127.1 (Ph); 88.1 (Cp); 48.5, 45.6 CH₂N). MS (EI), m/z (rel. int.(%)): 554 (0.1) (M^+); 526 $(0.1) [M-CO]^+; 498 (0.6) [M-2CO]^+; 470 (0.1) [M-$ 3CO]⁺; 186 (59) [FeCp₂]⁺.

4.2. Reaction of 2 with n-butyllithium

A suspension of 0.30 g (0.47 mmol) of 2-PF₆ in 5 ml of THF was cooled to -60° C. To this 0.2 ml of n-butyllithium (15% in n-hexane) were dropped within 6 min, and the mixture was allowed to warm to r.t. over a period of 24 h. The precipitate was separated and extracted with 4 ml of dichloromethane leaving 3-PF₆ as a red powder. From the dichloromethane solution major amounts of the educt 2-PF₆ were recovered.

Some more 3-PF_6 was precipitated from the red THF phase on addition of 4 ml of diethyl ether, and the clear supernatant solution was taken to dryness. The residue was then chromatographed on silica (2 × 15 cm-column) with light petroleum/ether (1/2) as eluent. A first pale yellow fraction contained phthalimine (5 mg), the second orange–red one contained **6** which after removal of the solvent remained as an orange–red powder.

3-PF₆: Yield 48 mg (15%). M.p. 215–216°C. IR (Nujol mull, cm⁻¹): 2005s, 1963m [ν (CO)_{term}]; 1834m [ν (μ -CO)]; 1789s [ν (C=N=C)]; 845s [ν (PF₆)]. ¹H NMR (δ , CD₃CN): 5.37, 5.12 (2s, Cp). MS (pos-FAB), m/z (rel. int. (%)): 690 (5) (M^+); 634 (2) [M-2CO]⁺; 324(5) [Fe₂(CN)Cp₂(CO)₂]⁺.

6: Yield 1 mg (0.3%). M.p. 65–66°C (dec.). IR (Nujol mull, cm⁻¹): 1994s, 1956m [ν (CO)_{term}]; 1774m [ν (μ -CO)]; 1731s [ν (C=O)_{ketone}]; 1680m [ν (C=O)_{acyl}]; 1655m [ν (μ -CN)]. MS (pos-FAB), m/z (rel. int. (%)): 542 (0.9) [M + H]⁺; 324 (4) [Fe₂(CN)Cp₂(CO)₂]⁺.

4.3. Reaction of 2 with NaCN

A mixture of 0.43 g (0.68 mmol) of 2-PF_6 and 0.033 g (0.68 mmol) of NaCN was stirred in 1,2dimethoxyethane (15 ml) for 14 h. The deep-red suspension was filtered through a G4 frit, the solid was recrystallized from THF/light petroleum and identified as the tetraferrio-azaallenium species 3-PF_6 by its IR spectrum. Yield 40 mg.

The red filtrate was cooled to -78° C causing precipitation of 20 mg of a colourless crystalline material which according to the IR spectrum was sodium hexafluorophosphate. On addition of light petroleum (3 ml) product 7 crystallized in deep-red lumps within 13 h at 0°C. Yield 5 mg (14%). M.p. 120-123°C. Anal. Calc. for $C_{23}H_{14}Fe_2N_2O_5$ (510.07 g mol⁻¹): C, 54.16; H, 2.77; N, 5.49. Found: C, 51.86; H, 3.09; N, 5.17%. IR (CH_2Cl_2, cm^{-1}) : 2166m [$v(CN)_{term}$]; 2007vs, 1971m $[v(CO)_{term}]$; 1805s,br, 1777w $[v(\mu-CO)]$; 1712s, 1702s $[\nu(C=O)_{acvl}]$. ¹H NMR (δ , CD₃CN): 7.80 (m_c, 4H, Ph); 5.10 (s, 10H, Cp). ${}^{13}C{H}$ NMR (δ , CD₂Cl₂): 264.1 (µ-CO); 210.2 (CO)_{term}; 134.5 (CN); 132.0, 123.7, 123.3 (Ph); 92.3 (Cp). MS (EI), m/z (rel. int. (%)): 482 (4) $[M-CO]^+$; 454 (9) $[M-2CO]^+$; 426 (66) $[M-3CO]^+$; 186 (100) [FeCp₂]⁺; 147 (16) [phthalimine]⁺.

4.4. Reaction of **2** with tetraethylammonium pentacarbonylcyanochromate, $NEt_4[Cr(CN)(CO)_5]$. Complex **9**

In total 7 ml of dichloromethane were added to a dry mixture of the reactants NEt₄[Cr(CN)(CO)₅] (0.28 g, 0.79 mmol) and $2-PF_6$ (0.50 g, 0.79 mmol), and the suspension was stirred at 32°C for 12 h. The solvent was removed in an oil vacuum, and the coppercoloured solid was extracted with 3 ml of ether. After filtration through a G4 frit small, deep violet-red parallelepipeds together with needle-like fragments crystallized from the deep-red solution at -30° C. Yield 15 mg (2%). M.p. 143°C (dec.). IR (KBr, cm⁻¹): 2137m-w [v(CN)_{term}]; 2060m, 1991sh, 1977vs, 1938vs, 1908vs, 1887vs $[v(CO)_{term}];$ 1820s $[v(\mu-CO)];$ 1713m-s [v(C=O)_{acvl}]. ¹H NMR (δ, CD₃CN): 8.32–8.14 (m_c, 4H, Ph); 5.00 (s, 5H, Cp); 4.82 (s, 4.9H, Cp). MS (pos-FAB), m/z (rel. int. (%)): 674 (1.7) (M^+); 534 (6) Table 3

Selected bond distances (Å) and bond angles (°), best planes and interplanar angles (°) of 10^{a}

Bond distances (Å) $W1-N2$ 2.15(2) C2-O2 1.19(3) $W1-C6$ 1.96(3) C3-O3 1.15(3) $W1-C7$ 1.93(2) C4-O4 1.11(3) $W1-C9$ 2.01(4) C6-O6 1.18(4) $W1-C10$ 1.92(2) C7-O7 1.21(3) $W1-C8$ 1.82(3) C9-O9 1.15(5) Fe1-Fe2 2.512(6) C10-O10 1.20(3) Fe1-C1 1.95(3) C8-O8 1.24(4) Fe1-C2 1.88(2) C11-O11 1.22(3) Fe1-C4 1.76(2) C12-O12 1.18(3) Fe2-C1 2.01(2) C11-C18 1.44(3) Fe2-C2 1.88(3) C12-C13 1.53(3) Fe2-C3 1.75(2) C13-C14 1.40(3) Fe2-C4 1.40(4) C15-C16 1.33(4) N1-C1 1.47(2) C14-C15 1.50(4) N1-C1 1.47(2) C14-C15 1.60(2) N1-C1 1.47(2) C14-C15 1.60(2)					
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Bond distances (Å	.)			
$\begin{array}{ccccccc} W1-C6 & 1.96(3) & C3-O3 & 1.15(3) \\ W1-C7 & 1.93(2) & C4-O4 & 1.11(3) \\ W1-C9 & 2.01(4) & C6-O6 & 1.18(4) \\ W1-C10 & 1.92(2) & C7-O7 & 1.21(3) \\ W1-C8 & 1.82(3) & C9-O9 & 1.15(5) \\ Fe1-Fe2 & 2.512(6) & C10-O10 & 1.20(3) \\ Fe1-C1 & 1.95(3) & C8-O8 & 1.24(4) \\ Fe1-C2 & 1.88(2) & C11-O11 & 1.22(3) \\ Fe1-C4 & 1.76(2) & C12-O12 & 1.18(3) \\ Fe2-C(P)^{b} & 2.11(3) & C1-C5 & 1.45(3) \\ Fe2-C1 & 2.01(2) & C11-C18 & 1.44(3) \\ Fe2-C2 & 1.88(3) & C12-C13 & 1.53(3) \\ Fe2-C3 & 1.75(2) & C13-C14 & 1.40(3) \\ Fe2-C(Cp)^{b} & 2.12(3) & C13-C18 & 1.35(4) \\ N1-C1 & 1.47(2) & C14-C15 & 1.50(4) \\ N1-C1 & 1.47(2) & C14-C15 & 1.50(4) \\ N1-C11 & 1.40(4) & C15-C16 & 1.33(4) \\ N1-C12 & 1.41(3) & C16-C17 & 1.44(3) \\ N2-C5 & 1.18(3) & C17-C18 & 1.40(4) \\ Bond angles (^{\circ}) \\ N2-W1-C8 & 177(1) & C1-N1-C11 & 127(2) \\ C6-W1-C9 & 176(1) & C11-N1-C12 & 108(2) \\ C7-W1-C10 & 176(1) & C11-N1-C12 & 108(2) \\ C7-W1-C10 & 176(1) & C11-C18-C13 & 107(2) \\ N1-C1-C5 & 104(2) & C12-C13-C18 & 110(2) \\ Fe1-C2-Fe2 & 84(1) & C13-C18-C17 & 121(2) \\ Fe1-C2-Fe2 & 84(1) & C13-C18-C17 & 123(2) \\ N1-C11-C18 & 111(2) & C16-C17-C18 & 115(3) \\ N1-C12-C13 & 105(2) & C41-O44-C411 & 116(3) \\ N1-C12-C13 & 105(2) & C42-C41-O44 & 106(3) \\ Best planes \\ I: Fe1, C1, Fe2 & III: N1, C11, C12, C13, C18 \\ II: Fe2, C2, Fe1 & IV: C13, C14, C15, C16, C17 \\ Interplanar angles (^{\circ}) \\ I/II: 163(1) & III/IV: 179.3(7) \\ \end{array}$	W1-N2	2.15(2)	C2–O2	1.19(3)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	W1-C6	1.96(3)	C3–O3 1.		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	W1-C7	1.93(2)	C4–O4	1.11(3)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	W1-C9	2.01(4)	C6–O6 1		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	W1-C10	1.92(2)	C7–O7 1.		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	W1-C8	1.82(3)	C9–O9	1.15(5)	
Fe1-C11.95(3)C8-O81.24(4)Fe1-C21.88(2)C11-O111.22(3)Fe1-C41.76(2)C12-O121.18(3)Fe1-C(Cp) b2.11(3)C1-C51.45(3)Fe2-C12.01(2)C11-C181.44(3)Fe2-C21.88(3)C12-C131.53(3)Fe2-C31.75(2)C13-C141.40(3)Fe2-C41.47(2)C14-C151.50(4)N1-C11.47(2)C14-C151.50(4)N1-C11.47(2)C14-C151.33(4)N1-C121.41(3)C16-C171.44(3)N2-C51.18(3)C17-C181.40(4)Bond angles (°)N2-W1-C8177(1)C1-N1-C11N2-W1-C8177(1)C1-N1-C13107(2)C6-W1-C9176(1)C11-N1-C12108(2)C7-W1-C10176(1)C11-C18-C13107(2)N1-C1-C5104(2)C12-C13-C18110(2)Fe1-C1-Fe278.9(8)C13-C14-C15110(2)Fe1-C2-Fe284(1)C13-C18-C17121(2)Fe1-C4-O4176(2)C14-C15-C16123(2)N1-C11-C18111(2)C16-C17-C18115(3)N1-C12-C13105(2)C41-O44-C411116(3)N1-C12-C13105(2)C41-O44-C411116(3)N1-C12-C13105(2)C41-O44-C411116(3)N1-C12-C13105(2)C41-O44-C411116(3)N1-C12-C13105(2)C41-O44-C411106(3)N1-C12-C13105(2)C42-C41-O44106(3) <t< td=""><td>Fe1–Fe2</td><td>2.512(6)</td><td>C10–O10</td><td>1.20(3)</td></t<>	Fe1–Fe2	2.512(6)	C10–O10	1.20(3)	
Fe1-C2 $1.88(2)$ C11-O11 $1.22(3)$ Fe1-C4 $1.76(2)$ C12-O12 $1.18(3)$ Fe1-C(Cp) b $2.11(3)$ C1-C5 $1.45(3)$ Fe2-C1 $2.01(2)$ C11-C18 $1.44(3)$ Fe2-C2 $1.88(3)$ C12-C13 $1.53(3)$ Fe2-C3 $1.75(2)$ C13-C14 $1.40(3)$ Fe2-C(Cp) b $2.12(3)$ C13-C18 $1.35(4)$ N1-C1 $1.47(2)$ C14-C15 $1.50(4)$ N1-C1 $1.47(2)$ C14-C15 $1.50(4)$ N1-C12 $1.41(3)$ C16-C17 $1.44(3)$ N2-C5 $1.18(3)$ C17-C18 $1.40(4)$ Bond angles (°) $N2-W1-C8$ $177(1)$ C1-N1-C11N2-W1-C8 $177(1)$ C1-N1-C11 $127(2)$ C6-W1-C9 $176(1)$ C11-N1-C12 $108(2)$ C7-W1-C10 $176(1)$ C11-C18-C13 $107(2)$ N1-C1-C5 $104(2)$ C12-C13-C18 $110(2)$ Fe1-C1-Fe2 $78.9(8)$ C13-C14-C15 $110(2)$ Fe1-C2-Fe2 $84(1)$ C13-C18-C17 $121(2)$ Fe1-C4-O4 $176(2)$ C14-C15-C16 $123(2)$ N1-C11-C18 $111(2)$ C16-C17-C18 $115(3)$ N1-C12-C13 $105(2)$ C41-O44-C411 $116(3)$ N1-C12-O12 $125(2)$ C42-C41-O44 $106(3)$ Best planesI:Fe1, C1, Fe2III: N1, C11, C12, C13, C18I: Fe2, C2, Fe1III: N1, C11, C12, C13, C18, C17Interplanar angles (°)III/IV: 179.3(7)	Fe1–C1	1.95(3)	C8–O8 1.		
Fe1-C41.76(2)C12-O121.18(3)Fe1-C(Cp) b2.11(3)C1-C51.45(3)Fe2-C12.01(2)C11-C181.44(3)Fe2-C21.88(3)C12-C131.53(3)Fe2-C31.75(2)C13-C141.40(3)Fe2-C(Cp) b2.12(3)C13-C181.35(4)N1-C11.47(2)C14-C151.50(4)N1-C11.47(2)C14-C151.50(4)N1-C121.41(3)C16-C171.44(3)N2-C51.18(3)C17-C181.40(4)Bond angles (°)N2-W1-C8177(1)C1-N1-C11N2-W1-C8177(1)C1-N1-C13107(2)C6-W1-C9176(1)C11-N1-C13107(2)N1-C1-C5104(2)C12-C13-C18110(2)Fe1-C1-Fe278.9(8)C13-C14-C15110(2)Fe1-C2-Fe284(1)C13-C18-C17121(2)Fe1-C4-O4176(2)C14-C15-C16123(2)Fe2-C3-O3175(2)C15-C16-C17123(2)N1-C11-C18111(2)C16-C17-C18115(3)N1-C12-C13105(2)C41-O44-C411116(3)N1-C12-O12125(2)C42-C41-O44106(3)Best planesI:Fe1, C1, Fe2III: N1, C11, C12, C13, C18I: Fe2, C2, Fe1III: N1, C11, C12, C13, C18II: Fe2, C2, Fe1II: II: I63(1)III/IV: 179.3(7)III/IV: I79.3(7)	Fe1–C2	1.88(2)	C11–O11 1.2		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Fe1–C4	1.76(2)	C12–O12	1.18(3)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Fe1–C(Cp) ^b	2.11(3)	C1–C5	1.45(3)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Fe2–C1	2.01(2)	C11–C18	1.44(3)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Fe2–C2	1.88(3)	C12–C13	1.53(3)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Fe2–C3	1.75(2)	C13–C14	1.40(3)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Fe2–C(Cp) ^b	2.12(3)	C13–C18	1.35(4)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N1-C1	1.47(2)	C14-C15	1.50(4)	
$\begin{array}{cccccccc} \mathrm{N1-C12} & 1.41(3) & \mathrm{C16-C17} & 1.44(3) \\ \mathrm{N2-C5} & 1.18(3) & \mathrm{C17-C18} & 1.40(4) \\ \hlinelength{Bond angles}(^{\circ}) & & & & \\ \mathrm{N2-W1-C8} & 177(1) & \mathrm{C1-N1-C11} & 127(2) \\ \mathrm{C6-W1-C9} & 176(1) & \mathrm{C11-N1-C12} & 108(2) \\ \mathrm{C7-W1-C10} & 176(1) & \mathrm{C11-C18-C13} & 107(2) \\ \mathrm{N1-C1-C5} & 104(2) & \mathrm{C12-C13-C18} & 110(2) \\ \mathrm{Fe1-C1-Fe2} & 78.9(8) & \mathrm{C13-C14-C15} & 110(2) \\ \mathrm{Fe1-C2-Fe2} & 84(1) & \mathrm{C13-C18-C17} & 121(2) \\ \mathrm{Fe1-C4-04} & 176(2) & \mathrm{C14-C15-C16} & 123(2) \\ \mathrm{Fe2-C3-03} & 175(2) & \mathrm{C15-C16-C17} & 123(2) \\ \mathrm{N1-C11-C18} & 111(2) & \mathrm{C16-C17-C18} & 115(3) \\ \mathrm{N1-C11-O11} & 123(2) & & & \\ \mathrm{N1-C12-O12} & 125(2) & \mathrm{C41-O44-C411} & 116(3) \\ \mathrm{N1-C12-O12} & 125(2) & \mathrm{C42-C41-O44} & 106(3) \\ \hline \hline \\ \hline \\ Best planes \\ \mathrm{I:} \ \mathrm{Fe1, C1, \ Fe2} & & \\ \mathrm{II: \ \mathrm{N1, \ C11, \ C12, \ C13, \ C18} \\ \mathrm{II: \ \mathrm{Fe2, \ C2, \ Fe1}} & & \\ \mathrm{III: \ \mathrm{N1, \ C13, \ C14, \ C15, \ C16, \ C17} \\ \hline \\ Interplanar \ angles \ (^{\circ}) \\ \mathrm{I/II: \ 163(1)} & & \\ \mathrm{III/IV: \ 179.3(7) \\ \hline \end{array}$	N1-C11	1.40(4)	C15-C16	1.33(4)	
N2-C51.18(3)C17-C181.40(4)Bond angles (°) $N2-W1-C8$ 177(1)C1-N1-C11127(2)C6-W1-C9176(1)C11-N1-C12108(2)C7-W1-C10176(1)C11-C18-C13107(2)N1-C1-C5104(2)C12-C13-C18110(2)Fe1-C1-Fe278.9(8)C13-C14-C15110(2)Fe1-C2-Fe284(1)C13-C18-C17121(2)Fe1-C4-O4176(2)C14-C15-C16123(2)Fe2-C3-O3175(2)C15-C16-C17123(2)N1-C11-C18111(2)C16-C17-C18115(3)N1-C12-C13105(2)C41-O44-C411116(3)N1-C12-O12125(2)C42-C41-O44106(3)Best planesII:Fe1, C1, Fe2III: N1, C11, C12, C13, C18I: Fe1, C1, Fe2III: N1, C11, C12, C13, C16, C17Interplanar angles (°)III/IV: 179.3(7)	N1-C12	1.41(3)	C16–C17	1.44(3)	
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N2-C5	1.18(3)	C17–C18	1.40(4)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Bond angles (°)				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N2-W1-C8	177(1)	C1-N1-C11	127(2)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C6-W1-C9	176(1)	C11–N1–C12 10		
$\begin{array}{cccccccc} \mathrm{N1-C1-C5} & 104(2) & \mathrm{C12-C13-C18} & 110(2) \\ \mathrm{Fe1-C1-Fe2} & 78.9(8) & \mathrm{C13-C14-C15} & 110(2) \\ \mathrm{Fe1-C2-Fe2} & 84(1) & \mathrm{C13-C18-C17} & 121(2) \\ \mathrm{Fe1-C4-O4} & 176(2) & \mathrm{C14-C15-C16} & 123(2) \\ \mathrm{Fe2-C3-O3} & 175(2) & \mathrm{C15-C16-C17} & 123(2) \\ \mathrm{N1-C11-C18} & 111(2) & \mathrm{C16-C17-C18} & 115(3) \\ \mathrm{N1-C11-O11} & 123(2) & & & \\ \mathrm{N1-C12-C13} & 105(2) & \mathrm{C41-O44-C411} & 116(3) \\ \mathrm{N1-C12-O12} & 125(2) & \mathrm{C42-C41-O44} & 106(3) \\ \hline \\ Best \ planes & & \\ \mathrm{I:}\ \mathrm{Fe1, C1, Fe2} & & \\ \mathrm{III: N1, C11, C12, C13, C18} \\ \mathrm{II: Fe2, C2, Fe1} & & \\ \mathrm{IV: C13, C14, C15, C16, C17} \\ \hline \\ Interplanar \ angles (^{\circ}) \\ \mathrm{I/II: 163(1)} & & \\ \mathrm{III/IV: 179.3(7)} \\ \end{array}$	C7-W1-C10	176(1)	C11–C18–C13 107		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N1-C1-C5	104(2)	C12–C13–C18 1100		
Fe1-C2-Fe2 84(1) C13-C18-C17 121(2) Fe1-C4-O4 176(2) C14-C15-C16 123(2) Fe2-C3-O3 175(2) C15-C16-C17 123(2) N1-C11-C18 111(2) C16-C17-C18 115(3) N1-C12-C13 105(2) C41-O44-C411 116(3) N1-C12-O12 125(2) C42-C41-O44 106(3) Best planes III: N1, C11, C12, C13, C18 II II: Fe2, C2, Fe1 IV: C13, C14, C15, C16, C17 Interplanar angles (°) I/II: 163(1) III/IV: 179.3(7) III	Fe1-C1-Fe2	78.9(8)	C13-C14-C15	110(2)	
Fe1-C4-O4 176(2) C14-C15-C16 123(2) Fe2-C3-O3 175(2) C15-C16-C17 123(2) N1-C11-C18 111(2) C16-C17-C18 115(3) N1-C11-O11 123(2) N1-C12-C13 105(2) C41-O44-C411 116(3) N1-C12-O12 125(2) C42-C41-O44 106(3) Best planes III: N1, C11, C12, C13, C18 II: Fe1, C1, Fe2 III: N1, C14, C15, C16, C17 Interplanar angles (°) I/II: 163(1) III/IV: 179.3(7)	Fe1-C2-Fe2	84(1)	C13-C18-C17	121(2)	
Fe2_C3-O3 175(2) C15-C16-C17 123(2) N1-C11-C18 111(2) C16-C17-C18 115(3) N1-C11-O11 123(2) 115(3) N1-C12-C13 105(2) C41-O44-C411 116(3) N1-C12-O12 125(2) C42-C41-O44 106(3) Best planes III: N1, C11, C12, C13, C18 II: Fe2, C2, Fe1 IV: C13, C14, C15, C16, C17 Interplanar angles (°) I/II: 163(1) III/IV: 179.3(7)	Fe1-C4-O4	176(2)	C14-C15-C16	123(2)	
N1-C11-C18 111(2) C16-C17-C18 115(3) N1-C11-O11 123(2) 105(2) C41-O44-C411 116(3) N1-C12-C13 105(2) C41-O44-C411 106(3) Best planes III: N1, C11, C12, C13, C18 11: Fe2, C2, Fe1 III: N1, C14, C15, C16, C17 Interplanar angles (°) III/IV: 179.3(7) III/V: 179.3(7)	Fe2-C3-O3	175(2)	C15-C16-C17	123(2)	
N1-C11-O11 123(2) N1-C12-C13 105(2) C41-O44-C411 116(3) N1-C12-O12 125(2) C42-C41-O44 106(3) Best planes III: N1, C11, C12, C13, C18 II: Fe1, C1, Fe2 III: N1, C11, C12, C13, C18 II: Fe2, C2, Fe1 IV: C13, C14, C15, C16, C17 Interplanar angles (°) III/IV: 179.3(7)	N1-C11-C18	111(2)	C16-C17-C18	115(3)	
N1-C12-C13 105(2) C41-O44-C411 116(3) N1-C12-O12 125(2) C42-C41-O44 106(3) Best planes III: N1, C11, C12, C13, C18 III: Fe2, C2, Fe1 IV: C13, C14, C15, C16, C17 Interplanar angles (°) III/IV: 179.3(7) III/V: 179.3(7)	N1-C11-O11	123(2)			
N1-C12-O12 125(2) C42-C41-O44 106(3) Best planes III: N1, C11, C12, C13, C18 II: Fe1, C1, Fe2 III: N1, C11, C12, C13, C18 II: Fe2, C2, Fe1 IV: C13, C14, C15, C16, C17 Interplanar angles (°) III/IV: 179.3(7)	N1-C12-C13	105(2)	C41-O44-C411	116(3)	
Best planes I: Fe1, C1, Fe2 III: N1, C11, C12, C13, C18 II: Fe2, C2, Fe1 IV: C13, C14, C15, C16, C17 Interplanar angles (°) III/IV: 179.3(7)	N1-C12-O12	125(2)	C42-C41-O44	106(3)	
I: Fe1, C1, Fe2 III: N1, C11, C12, C13, C18 II: Fe2, C2, Fe1 IV: C13, C14, C15, C16, C17 Interplanar angles (°) III/IV: 179.3(7)	Best planes				
II: Fe2, C2, Fe1 IV: C13, C14, C15, C16, C17 Interplanar angles (°) III/IV: 179.3(7)	I: Fe1, C1, Fe2		III: N1, C11, C12, C13, C18		
Interplanar angles (°) I/II: 163(1) III/IV: 179.3(7)	II: Fe2, C2, Fe1		IV: C13, C14, C15, C16, C17		
I/II: 163(1) III/IV: 179.3(7)	Interplanar angles (°)				
	I/II: 163(1)		III/IV: 179.3(7)		

^a E.s.d.s are given in parentheses, see Fig. 2 for atomic numbering. ^b Average value.

 $[M-5CO]^+$; 399 (29) $[M-8CO-CrCNH]^+$; 268 (13) $[Fe_2Cp_2CN]^+$.

After purification by recrystallization from dichloromethane the residue proved to be pure $3-PF_6$.

4.5. Reaction of **2** with tetraethylammonium pentacarbonylcyanotungstate, $NEt_4[W(CN)(CO)_5]$. Complex **10**

Mixing of the dry components 2-PF_6 (0.48 g, 0.76 mmol) and NEt₄[W(CN)(CO)₅] (0.37g, 0.77 mmol) was followed by the addition of 7 ml of dichloromethane and warming of the reaction mixture to 35°C. After 13 h the solvent was removed in an oil vacuum, and the

resulting copper-coloured solid was extracted with 4 ml of ether. Within 18 h at -30° C, the product crystallized in deep-red rhomboids and blocks. Yield 70 mg (11%). M.p. 149-151°C. Anal. for Calc. $C_{28}H_{14}Fe_2N_2O_{10}W$ (833.96 g mol⁻¹): C, 40.33; H, 1.69; N, 3.36. Found: C, 41.35; H, 2.81; N, 3.24%. IR (KBr, cm⁻¹): 2175m [v(CN)_{term}]; 2068m, 2008s, 1910vs,br, 1907vs,br [$\nu(CO)_{term}$]; 1809s [$\nu(\mu$ -CO)]; 1713m-s $[\nu(C=O)_{acvl}]$. ¹H NMR (δ , CD₃CN): 7.82–7.16 (m, 4H, Ph); 5.20, 4.85 (2s, 10H, Cp). ${}^{13}C{H}$ NMR (δ , CD₃CN): 262.3 (µ-CO); 211.1 (CO)_{term}; 202.0 (WCO)ax; 197.3 (WCO)eq; 169.3 (C=O)acyl; 137.7 (CNW); 135.5, 132.2, 121.4 (Ph); 107.7, 92.6 (Cp). MS (pos-FAB), m/z (rel. int. (%)): 834 (1) (M^+); 806 (8) $[M-CO]^+$; 722 (4) $[M-4CO]^+$; 638 (4) $[M-7CO]^+$; 610 (14) [M-8CO]⁺.

4.6. Reaction of 3 with n-propylamine. Complex 11

n-Propylamine (0.016 ml, 0.2 mmol) was added to a suspension of **3**-BF₄ (0.16 g, 0.2 mmol) in 3 ml of 1,4-dioxane, and the mixture was stirred at 108°C for 12 h. After cooling to r.t. the red solution was filtered and mixed with 5 ml of ether to remove unreacted **3**-BF₄. Upon layering with another 5 ml of ether the product separated overnight as a red powder. Yield 30 mg (15%). M.p. 115–116°C. IR (KBr, cm⁻¹): 2158m [ν (CN)_{term}]; 2055w, 2001s, 1964m-w [ν (CO)_{term}]; 1810sh [ν (μ -CO)]; 1768vs [ν (C=N=C)]; 1048vs [ν (BF₄)]. ¹H NMR (δ , CD₃CN): 5.33, 5.21, 5.12 (3s, 20H, Cp). MS (pos-FAB), m/z (rel. int. (%)): 731 (20) (M^+); 703 [M-CO]⁺; 675 (11) [M-2CO]⁺; 470 (3) [M-5CO–FeCp]⁺.

4.7. Reaction of 3 with 2-methoxyethylamine. Complex 12

A mixture of 0.40 g (0.52 mmol) of $3-BF_4$ and 0.05 ml (0.52 mmol) of 2-methoxyethylamine in 8 ml of 1,4-dioxane was stirred at 108°C for 16 h after which time it was allowed to cool to r.t. The solid that had separated from the solution was identified as unreacted starting material (140 mg). A second crop of 3-BF₄ formed on addition of 12 ml of ether to the deep red solution and was filtered off. Layering with 10 ml of light petroleum of the solution caused crystallization of the product as a fine red-violet powder. Yield 10 mg (2%). M.p. 110-115°C. IR (KBr, cm⁻¹): 2155m-w, 2091w [v(CN)_{term}]; 2055w, 2001s, 1961w [v(CO)_{term}]; 1768vs [v(C=N=C)]; 1051s [$v(BF_4)$]. ¹H NMR (δ , CDCl₃): 5.28 (s, 5H, Cp), 5.08 (s, 10H, Cp), 4.84 (s, 5H, Cp); 3.72 (s, 3H, OMe); 3.48 (m_c, 4H, 2CH₂). MS (pos-FAB), m/z (rel. int. (%)): 747 (39) (M^+); 719 (3) $[M-CO]^+$; 691 (26) $[M-2CO]^+$; 663 (3) $[M-3CO]^+$; 634 (14) [*M*-CO-C₄H₇NO].

4.8. Reaction of 3 with 2-phenylethylamine. Complex 13

To a stirred suspension of 3-BF₄ (0.27 g, 0.35 mmol) in 5 ml of 1,4-dioxane was added phenylethylamine (0.05 ml, 0.40 mmol) within 3 min. The suspension was then heated to 114°C for 11 h. When it cooled to r.t. the suspension was filtered through a G4 frit to afford 190 mg of pure $3-BF_4$. Treatment with 5 ml of ether followed by 7 ml of light petroleum as described above (Sections 4.6 and 4.7) resulted in 5 mg (16%) of a wine-red powder. M.p. 110–111°C. IR (KBr, cm^{-1}): 2149m-w $[v(CN)_{term}];$ 2055w, 2001s, 1965s-m $[v(CO)_{term}];$ 1763vs [v(C=N1=C)]; 1083m, 1048s $[v(BF_4)]$. MS (pos-FAB), m/z (rel. int. (%)): 793 (1) (M^+) ; 737 (0.5) $[M-2CO]^+$.

4.9. Reaction of **3** with sodium cyanide. Complex **14** by substitution

The dry reactants $3-PF_6$ (0.63 g, 0.75 mmol) and NaCN (0.04 g, 0.81 mmol) were thoroughly mixed, then 1,4-dioxane (10 ml) was added. The suspension was stirred for 15 h at 128°C after which time the solvent was removed in vacuo. From the red solid the product was extracted with a total of 30 ml of dichloromethane. The burgundy-red opalescent solution was filtered through a G4 frit which was charged with a thin layer of silica. Addition to the solution of an equal amount of ether causes the microcrystalline product to separate overnight. Yield 20 mg (4%). M.p. 245°C (dec.). IR (KBr, cm^{-1}): 2082m [ν (CN)_{term}]; 2001s, 1966s [v(CO)_{term}]; 1812w [v(µ-CO)]; 1757vs, br [v(C=N=C)]; (CH₂Cl₂, cm⁻¹): 2090w $[v(CN)_{term}];$ 2005m, 1975m [ν (CO)_{term}]; 1813w [ν (μ -CO)]; 1764s [v(C=N=C)]. ¹H NMR (δ , CD₃CN): 5.17 (s, 10H, Cp), 4.87 (s, 10H, Cp). MS (pos-FAB), m/z (rel. int. (%)): 689 (0.9) $({M + H}^+)$; 661 $[{M + H}^-CO]^+$; 633 $[{M + H} - 2CO]^+$. MS (neg-FAB), m/z (rel. int. (%)): $660 (14) [M-CO]^-; 632 (14) [M-2CO]^-; 604 (19)$ [M-3CO]⁻; 483 (12) [M-3CO-FeCp]⁻; 362 (9) [M- $3CO-Fe_2Cp_2]^-$.

4.10. Reaction of 3 with sodium amide. Complex 14 by $CO \rightarrow CN^{-}$ interconversion

Sodium amide (0.08 g, 1.93 mmol) was added in small doses to a suspension of 3-BF_4 (1.00 g, 1.29 mmol) in 17 ml of 1,4-dioxane and the mixture was stirred for 21 h at 104°C. The still hot suspension was then filtered through a G4 frit. After cooling to r.t. the filtrate was mixed with ether (15 ml) in order to remove some dissolved 3-BF_4 . Layering of the solution with light petroleum (10 ml) overnight resulted in the precipitation of a violet powder which was washed with more light petroleum and dried in vacuo. Yield 80 mg (9%). For further data, cf. Section 4.9.

Table 4						
Crystallographic d	lata collection	parameters	of 7,	9	and	10

	7	9	10
Crystal data			
Formula	C ₂₃ H ₁₄ Fe ₂ N ₂ O ₅	C ₂₇ H ₁₄ CrFe ₂ N ₂ O ₉	$C_{28}H_{14}Fe_2N_2O_{10}W + C_4H_{10}O$
Molecular weight (g mol^{-1})	510.07	674.12	908.08
Crystal size	$0.60 \times 0.25 \times 0.32$	$0.275\times0.075\times0.05$	$0.35 \times 0.28 \times 0.15$
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$ (no. 14)	<i>P</i> 1 (no. 2)	<i>C</i> 2/ <i>c</i> (no. 15)
Cell parameters			
a (pm)	1408.3(2)	1059.8	3374.1(4)
b (pm)	1224.1(1)	1208.3	1121.3(2)
<i>c</i> (pm)	1182.2(1)	1244.1	1921.5(3)
α (°)	90.0	105.15	90.0
β (°)	94.38(3)	94.81	122.33(1)
γ (°)	90.0	115.35	90.0
$U (10^6 \text{ pm}^3)$	2332.0(5)	1354.26	6143.02
Ζ	4	2	8
$D_{\rm c} \ ({\rm g} \ {\rm cm}^{-3})$	1.453	1.653	1.963
Data collection and refinement parameters			
Radiation, λ (pm)	graphite-monochron	nated Mo Ka, 71.069	
Temperature (K)	293	293	293
Scan mode	ω –2 θ scan	ω scan	ω –2 θ scan
2θ limits (°)	$4 \leq 2\theta \leq 40$	$4 \leq 2\theta \leq 50$	$4 \leq 2\theta \leq 44$
Total no. reflections	2136	3767	3016
No. data $[I \leq 2\sigma(I)]$	1700	2230	1884
No. parameters	284	370	198
R ^a	0.080	0.057	0.070
R _w ^b	0.101	0.062	0.042
Highest residual electron-density peaks $(10^{-6} \text{ e pm}^{-3})$	1.0 / - 1.1	0.9 / -1.5	1.9/-3.4

^a $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|.$

^b $R_{\rm w} = [\Sigma(w ||F_{\rm o}| - |F_{\rm c}||^2) / \Sigma(w |F_{\rm o}|^2)]^{1/2}, w = 1.0$ (unit weights).

4.11. Reaction of **3** with trimethylphosphite. Complex **15**

To 3-BF₄ (0.20 g, 0.26 mmol) suspended in 1,4dioxane (4 ml) trimethylphosphite (0.1 ml, 0.8 mmol) was added dropwise within a few minutes. The red suspension was kept stirring at 116°C for 14 h after which time it was allowed to cool and filtered through a G4 frit. The filtrate was layered with 5 ml of light petroleum. Within 14 h a violet powder had separated which was washed with a small amount of ether and dried in vacuo. Yield 1 mg (0.4%). M.p. 120–121°C. Anal. Calc. for $C_{32}H_{38}BF_4Fe_4NO_{10}P_2$ (968.78 g mol⁻¹): C, 39.67; H, 3.95; N, 1.44. Found: C, 40.98; H, 5.60; N, 1.39%. IR (KBr, cm⁻¹): 1994s, 1962vs $[v(CO)_{term}]$; 1748vs, br [v(C=N=C)]; 1177s, 1121s [v(C-O)]; 1049s $[v(BF_4)]$; 1018s [v(P-O)]. ¹H NMR (δ, CDCl₃): 5.02, 4.88 (2s, 20H, Cp); 3.58 (s, 18H, Me). MS (pos-FAB), m/z (rel. int. (%)): 882 (52) (M^+) ; 730 (10) $[M-CO-P(OMe)_3]^+$; 245 (33) $[FeCp{P(OMe)_3}]^+$.

4.12. Reactions of **3** with diamines. Complexes **16** and **17**

A slight excess of 1,2-diaminoethane (0.05 ml, 0.61 mmol) was added dropwise to a suspension of 3-BF_4 (0.40 g, 0.5 mmol) in 1,4-dioxane (8 ml), and the mixture was heated to about 110°C. After 15 h the red suspension was allowed to cool to r.t. and was filtered (G4). The filtrate was slightly concentrated and layered with ether whereupon the yellow-ochre product (16) crystallized.

The reaction with 1,4-diaminobutane was carried out in the same way to give 17. The main product (97 mg) was Fp_2 .

16: Yield 20 mg (16%). M.p. 132°C. IR (KBr, cm⁻¹): 3230s [ν (NH)]; 2083vs [ν (CN)_{term}]; 1931vs, 1896vw [ν (CO)_{term}]; 1514s [ν (N-C-N) = δ (NH)]. MS (pos-FAB), m/z (rel. int. (%)): 246 (4) [M + H]⁺; 217 (6) [M-CO]⁺; 191 (100) [M-CO-CN]⁺; 71 (37) [C₃H₆N₂]⁺.

17: Yield 10 mg (8%). M.p. 100–101°C. IR (KBr, cm⁻¹): 3404m, 3274m [v(NH)]; 2076s [v(CN)_{term}];

1947s, 1881vw [ν (CO)_{term}]; 1535m, 1516m-s [ν (N–C– N) + δ (NH)]. MS (pos-FAB), m/z (rel. int. (%)): 274 (100) [M + H]⁺; 245 (81) [M–CO]⁺; 219 (91) [M– CO–CN]⁺; 99 (48) [C₅H₁₁N₂]⁺.

4.13. Reaction of 3 with pyrrolidine. Complex 18

A suspension of **3**-BF₄ (0.30 g, 0.40 mmol) in 7 ml of 1,4-dioxane was reacted with pyrrolidine (55 mg, 0.8 mmol) at 105°C. After 13 h the solvent was removed and the red residue was washed several times with light petroleum. By treating the residue with light petroleum/ether (1/4) 40 mg of Fp₂ were extracted. Recrystallization from THF/ether gave the known product. Yield 2.1 mg (2%). M.p. 190–194°C. IR (KBr, cm⁻¹): 2018vs, 1999s [ν (CO)_{term}]; 1818s [ν (μ -CO)]; 1591s [ν (μ -CN <)]; 1077s, 1051s [ν (BF₄)]. MS (pos-FAB), m/z (rel. int. (%)): 408 (13) [M-3CO]⁺.

4.14. X-ray structure determinations

Single crystals of 7 were obtained by layering a solution in 1,2-dimethoxyethane with light petroleum, those of 9 and 10 by cooling their etheral solution to -30° C. The latter two were mounted in glass capillaries to prevent oxidative decomposition. The crystal symmetries and approximate cell parameters were determined by means of Weissenberg photographs.

The intensity data of compound 9 were collected on a STOE four-circle diffractometer, those of 7 and 10 on a Nonius CAD 4. All crystal structures were solved by direct methods and refined by full-matrix least-squares calculations based on $\Sigma w(|F_o| - |F_c|)^2$ initially with isotropic, then with anisotropic thermal parameters for all non-hydrogen atoms.

Calculations were carried out on a VAX computer using the programs SHELX-86 [22], XTAL 3.0 [23], DI-FABS [24] and SCHAKAL-88 [25]. Table 4 contains additional crystal and data collection parameters; selected bond lengths and angles are listed in Tables 1–3. For further information, see Section 5.

5. Supplementary material

Further details of the crystal structures may be obtained upon request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlichtechnische Information mbH, D-76344 Eggenstein-Leopoldshafen (Germany), giving reference to the depository number CSD 59463 and citing the authors and this paper.

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