DALTON

Selective C–C bond formation at diiron μ-aminocarbyne complexes†

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The reactions of $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ (Cp = η-C_5H_5, R = Me **2a** or CH_2Ph **2b**) with a variety of carbon nucleophiles result in C–C bond formation at different sites of the molecules depending on the nature of the carbanions: (*i*) R′Li (R′ = Me, Bu^n or Ph) and R′MgCl (R′ = Me, CH_2Ph or Pr^i) added at the Cp ligand giving η^4-cyclopentadiene complexes $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)_2(\eta^4\text{-}C_5H_5R')(Cp)]$ **3**; (*ii*) $Li_2Cu(CN)R'_2$ (R′ = Me or Bu^n) and LiC≡CR′ (R′ = Ph or *p*-tolyl) afforded the stable acyl complexes $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)\{C(O)R'\}(Cp)_2]$ **4** and $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)\{C(O)C{\equiv}CR'\}(Cp)_2]$ **5**, respectively. With R ≠ Me the NMR spectra of type **3**–**5** derivatives show the presence of two isomers arising from the double-bond character of the μ-C=N group ascertained from the crystal structure of $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)\{C(O)Bu^n\}(Cp)_2]$ **4b**. The structural study reveals the presence of interligand interactions involving the acyl oxygen and the μ-C=NMe_2 moiety which is also in accord with an extended-Hückel calculation of the charge distribution.

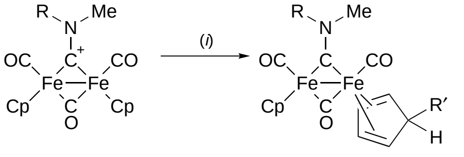
A number of new C–C bond forming reactions which take advantage of the strong electrophilic character of the bridging carbyne ligand in $[Fe_2(\mu\text{-}CR)(\mu\text{-}CO)(CO)_2(Cp)_2]^+$ (Cp = η^5-C_5H_5; R = H or alkyl) have been reported.[1] They are based upon nucleophilic addition that invariably involves the μ-CR unit. By contrast, our studies have shown that carbon nucleophiles react with the thiocarbyne complex $[Fe_2(\mu\text{-}CSMe)(\mu\text{-}CO)(CO)_2(Cp)_2]^+$ **1** generating C–C bonds at a number of different sites. These include the C_5H_5 ring[2] (Grignard reagents), terminal CO[3] (thienyllithium and phenylacetylide reagents), and the μ-carbyne carbon (reactions with organocopper nucleophiles).[3] Moreover nucleophilic attack at CO has been shown[3,4] to promote the formation of another C–C bond *via* $C(O)R^-$–μ-CSMe coupling, affording alkylidene complexes of the type $[Fe_2\{\mu\text{-}C(SMe)C(O)R\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R = H, OEt, CCPh or C_4H_3S).

In view of the fact that C–C bond forming reactions in binuclear transition-metal complexes are of considerable interest as models of related processes occurring on metal surfaces,[5] we have recently extended our studies[6] on the reaction of the bridging aminocarbyne complexes $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ (R = Me **2a**,[7] CH_2Ph **2b**[8]) with 2-thienyllithium. Compounds **1** and **2** are directly related, both presenting relevant π interaction between the bridging carbyne carbon and the adjacent π-donor heteroatom. Synthetic procedures to generate type **2** complexes and some of their spectroscopic features have been reinvestigated.[7] Some reactions of **2** with nucleophiles, mostly directed to replace the CO ligand[9] or give addition at the bridging carbyne carbon,[10] have also been described. Herein we report on the reactions of **2a** and **2b** with several carbon nucleophiles including organo-magnesium, -copper and -lithium reagents. All give selective addition at the CO or Cp ligands. Together with the spectroscopic characterization, an X-ray crystallographic study of $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)\{C(O)Bu^n\}(Cp)_2]$ **4b** has unambiguously established the molecular structure of the acyl derivative.

Results and Discussion

Addition at the Cp ring

The reactions of complexes **2a** and **2b** with organolithium reagents (LiR′) in thf solution at −40 °C result in the formation of the η^4-cyclopentadiene complexes $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)_2(\eta^4\text{-}C_5H_5R')(Cp)]$ (**3a**–**3f**) (Scheme 1). These complexes have been isolated after column chromatography in about 70–80% yield, and characterized by elemental analyses and spectroscopic methods.



R = Me **2a** or CH_2Ph **2b**

from R′Li			from R′MgCl		
	R	R′		R	R′
3a	Me	Me	**3a**	Me	Me
3b	Me	Bu^n	**3g**	Me	CH_2Ph
3c	Me	Ph	**3h**	Me	Pr^i
3d	CH_2Ph	Me	**3i**	CH_2Ph	CH_2Ph
3e	CH_2Ph	Bu^n			
3f	CH_2Ph	Ph			

Scheme 1 (*i*) R′Li or R′MgCl

The IR spectra of type **3** complexes exhibit a ν(CO) band pattern (*e.g.* for **3a** in CH_2Cl_2: 1959, 1921 and 1771 cm^{-1}) which is consistent with the presence of two terminal and one bridging CO ligand. The stretching vibration of the μ-C–N(Me)R falls in the expected range (1570–1630 cm^{-1}). The absence of the characteristic IR absorption of the cyclopentadiene H-*exo* atom around 2750 cm^{-1} suggests that R′ addition has occurred at the *exo*-side of the C_5H_5 ring, as found in related Cp addition reactions.[3,11] The ^1H NMR spectra of **3** generally show five peaks for the diastereotopic C_5H_5R ring protons (*e.g.* for **3a**: δ 4.61, 4.22, 3.51, 3.43, 3.18). The corresponding C_5H_5R ring carbons show five distinct signals in the ^{13}C NMR spectra (*e.g.* for **3a**: δ 88.2, 84.6, 84.4, 70.3, 70.1). Owing to the differences between the Cp and η^4-C_5H_5R' ligands, the Fe atoms are non-equivalent and the two N-bonded methyl groups in **3a**–**3c** originate separate equally intense singlets. One singlet signal due to the Cp protons is also observed in both the ^1H and ^{13}C NMR spectra of compounds **3a**–**3c** [*e.g.* for **3a**: δ 4.66 (^1H) and 85.3 (^{13}C)]. These observations indicate that, in spite of the chiral nature of both Fe atoms, the complexes **3a**–**3c** exist as single species in solution, presumably the *cis* isomer.[8,10] By contrast the NMR

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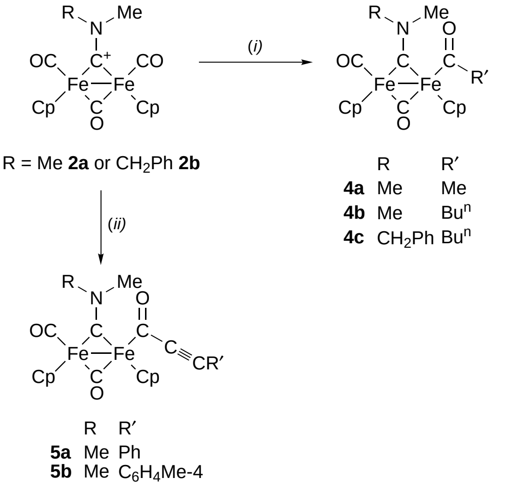
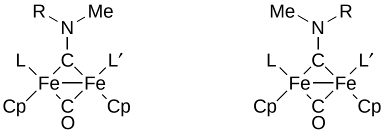
† *Non-SI unit employed*: eV ≈ 1.602 × 10^{-19} J.



Scheme 2 (*i*) $Li_2Cu(CN)R'_2$; (*ii*) LiC≡CR′



α and β forms

spectra of **3d**–**3f**, which contain the μ-CN(Me)CH$_2$Ph ligand, clearly show two unequal sets of resonances, indicating the presence of two isomeric forms. For example the ^{1}H NMR spectrum of **3d** exhibits two Cp signals, δ 4.73 and 4.64, and two NMe singlets, δ 3.74 and 3.64, of intensity ratio about 5 : 1. These isomers arise from the different orientations of R and R′ with respect to the non-equivalent Fe atoms, caused by restricted rotation around the μ-C=N bond. Analogous isomeric forms have been previously observed in related complexes of the type [Fe$_2$(Cp)$_2$LL′(μ-CO){μ-CN(Me)R}] (L = CO, L′ = CNR[7] or CN[9]) and indicated as α and β isomers.

Organomagnesium reagents (R′MgCl, R′ = Me or CH$_2$Ph), like LiR′, react with **2** to form the η^4-cyclopentadiene complexes [Fe$_2${μ-CN(Me)R}(μ-CO)(CO)$_2$(η^4-C$_5$H$_5$R′)(Cp)] (**3a**, **3g**–**3i**) (Scheme 1). The reactions, that have been carried out in tetrahydrofuran (thf) solution at 0 °C, afforded **3a**, **3g**–**3i**, as crystalline solids, in about 50% yield. Although yields are lower than those of the corresponding reactions with LiR, even in this case, type **3** compounds are the only observed reaction products. The spectroscopic properties of complexes **3g** and **3h** (see Experimental section) are in agreement with those discussed above for **3a**–**3c**. Compound **3i**, that differs from **3g** in having the unsymmetrically N-substituted μ-CN(Me)CH$_2$Ph ligand in place of μ-CN(Me)$_2$, shows the presence, in the NMR spectra, of the α and β isomeric forms (see Experimental section).

Finally it is worth mentioning that a common feature for all complexes **3a**–**3i** is the ^{13}C resonance due to the carbyne carbon of the μ-CN(Me)R ligand, that falls in the typical low-field shifted range around δ 330.

Addition at the CO ligand

Treatment of complexes **2a** and **2b**, in thf at −40 °C, with Li$_2$Cu(CN)R′$_2$, affords the acyl complexes [Fe$_2${μ-CN(Me)R}(μ-CO)(CO){C(O)R′}(Cp)$_2$] (R = R′ = Me **4a**; R = Me, R′ = Bu^n **4b**; R = CH$_2$Ph, R′ = Bu^n **4c**) which have been isolated in about 70% yield after column chromatography (Scheme 2).

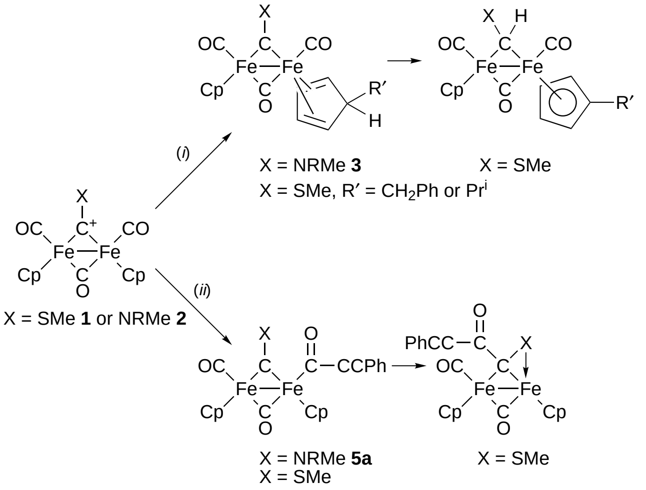
The IR spectra of **4a**–**4c**, in CH$_2$Cl$_2$ solution, exhibit one terminal and one bridging carbonyl absorption (*e.g.* for **4a** at 1963 and 1773s cm^{-1}, respectively) and a ν(COR) band at about 1600 cm^{-1}. Two distinct NMR signals, of the same intensity, are expected for the non-equivalent Cp groups of **4a** and **4b**, unless they are fortuitously coincident. Indeed two signals are shown in the ^{13}C NMR spectra (*e.g.* for **4a**: δ 89.1, 86.8), but only one, somewhat broad, Cp resonance appears in the corresponding ^{1}H NMR spectra. Each of the non-equivalent N-bonded methyl groups gives rise to a singlet resonance (*e.g.* for **4a**: δ 4.04 and 4.00). Key spectral features, in the ^{13}C NMR spectra, are the resonances of the aminocarbyne carbon, at about δ 330 and those attributable to the acyl carbon, around δ 268. The molecular structure of **4b** has been determined by an X-ray diffraction study (see later). While **4a** and **4b** consist of one single isomer in solution, the ^{1}H NMR spectrum of **4c**, containing the bridging amino carbyne ligand μ-CN(Me)CH$_2$Ph reveals, as expected, two sets of unequal resonances due to the presence of the α and β isomers in about 1 : 1 ratio.

The reactions between thf solutions of **2a**, at −20 °C, and LiC≡CR′ (R = Ph or *p*-tolyl) have been investigated. The complexes [Fe$_2${μ-CN(Me)R}(μ-CO)(CO){C(O)C≡CR′}(Cp)$_2$] (R′ = Ph **5a** or *p*-tolyl **5b**) have been obtained in about 50% yield as crystalline solids after separation by column chromatography. By contrast with the above described reactions of alkyl- and aryl-lithium, lithium acetylides attack the CO instead of the Cp ligand, behaving like 2-thienyllithium (Lith), which we have found to form the corresponding acyl complex [Fe$_2${μ-CN(Me)R}(μ-CO){C(O)th}(CO)$_2$(Cp)$_2$].[6] The lower basicity (or the softer nucleophilic character) of LiC≡CR′ and Lith, compared to the alkyl- or aryl-lithium reagents, should explain why they resemble the organocopper nucleophiles, displaying the same preference for the addition at the CO. The characterization of **5a** and **5b** has been straightforward since their spectroscopic properties are similar to those of the related complexes **4a** and **4b** (see Experimental section). The presence of the terminally co-ordinated C(O)C≡CR′ group is indicated by the occurrence of infrared absorptions at 2161 [ν(C≡C)] and 1573 cm^{-1} [ν(CO)] and by the observation, in the ^{13}C NMR, of resonances due to C≡C (δ 91.7, 88.2 for **5a**) and C(O) (δ 251.8 for **5a**) in addition to those attributable to the aromatic carbons (usual range δ 140–120).

The reactions of [Fe$_2${μ-CN(Me)R}(μ-CO)(CO)$_2$(Cp)$_2$]SO$_3$CF$_3$ **2a** and **2b** with carbon nucleophiles result in the formation of C–C bonds *via* addition at the C$_5$H$_5$ ring (Grignard reagents) or at the carbonyl ligand (organocopper and acetylide reagents). Neither displacement of the CO nor addition at the μ-carbyne carbon has been observed, although the latter are known reactions in diiron aminocarbyne chemistry.[9,10] Several factors may exert a regio- and stereo-chemical control on the reactions of nucleophiles with metal carbonyl complexes bearing other π-acid ligands,[12] but in our case the site of the nucleophilic attack seems to be determined by the nature of the reagent. Indeed the addition of an alkyl group can be selectively directed to the Cp or carbonyl ligands of **2** simply by using the appropriate Grignard or organocopper reagent, respectively.

The reactivity of **2a** and **2b** with carbon nucleophiles can be compared with that of the recently reported[3] thiocarbyne **1**. The μ-CSMe ligand appears more reactive than μ-CN(Me)R toward the organocopper nucleophiles. In fact Li$_2$Cu(CN)R′$_2$ reagents are known to attack the bridging thioalkylidyne ligand of **1**, affording μ-vinylidene and μ-alkylidene products,[3] whilst, in the case of **2** the addition occurs selectively at the CO ligand leaving the μ-CN(Me)R ligand intact. Such a difference should be the consequence of the stronger π interaction between the carbyne carbon and the adjacent N atom in μ-CN(Me)R compared to μ-CSMe. The strength of this interaction is well documented by a number of structural data (short C=N bond distances in the range 1.28–1.30 Å)[13] and by the absence of free rotation about C=N bond that is responsible for the observed α and β isomeric forms in complexes **3g**–**3i** and **4**.

The cationic carbyne complexes **2**, as well as **1**, react with Grignard reagents to give Cp ring addition products, but a significant difference can be envisaged in the relative stability of the complexes [Fe$_2$(μ-CX)(μ-CO)(CO)$_2$(η^4-C$_5$H$_5$R′)(Cp)] [X =



Scheme 3 (*i*) R′MgX; (*ii*) LiCCPh

N(Me)R or SMe] (Scheme 3). Whereas type **3** complexes [X = N(Me)R] are fairly stable, the corresponding thiocarbynes $[Fe_2(\mu\text{-}CSMe)(\mu\text{-}CO)(CO)_2(\eta^4\text{-}C_5H_5R')(Cp)]$ have been shown[2,3] to undergo hydrogen migration from the $\eta^4\text{-}C_5H_5R'$ ring to the bridging carbyne carbon and generate the alkylidene complexes $[Fe_2\{\mu\text{-}C(H)SMe\}(\mu\text{-}CO)(CO)_2(\eta^5\text{-}C_5H_4R')(Cp)]$. The same stability trend has been found in the compounds obtained by nucleophilic attack at the terminal CO of **1** and **2**. The μ-aminocarbyne complexes $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)\{C(O)R'\}(Cp)_2]$ **4** and **5** can be isolated in good yields whilst the corresponding thiocarbynes $[Fe_2\{\mu\text{-}CSMe\}(\mu\text{-}CO)(CO)\{C(O)R'\}(Cp)_2]$ are supposed reaction intermediates, which finally afford the μ-alkylidene derivatives $[FeFe\{\mu\text{-}C(COR')SMe\}(\mu\text{-}CO)(CO)(Cp)_2]$ *via* C(O)R′–alkylidyne coupling (Scheme 3).[3,4]

The different behavior can be ascribed to several factors. Among them, the double-bond character of the μ-C=N(Me)R interaction mentioned above should result in a less favorable aminocarbyne to aminocarbene ligand conversion with respect to the corresponding thiocarbyne to thiocarbene transformation. Furthermore the co-ordination of the sulfur to the Fe atom plays an important role in promoting the acyl–CSMe migratory coupling that accounts for the transformation of $[Fe_2(\mu\text{-}CSMe)(\mu\text{-}CO)(CO)\{C(O)CCPh\}(Cp)_2]$ into $[FeFe\{\mu\text{-}C[C(O)CCPh]SMe\}(\mu\text{-}CO)(CO)(Cp)_2]$ (Scheme 3). The absence of a corresponding μ-CN(Me)R–acyl ligand coupling in complexes **4** and **5** may also be due to the lower tendency of the nitrogen, compared to sulfur, to co-ordinate to the Fe atom. In fact bridging thiocarbene ligands frequently adopt an η^2 co-ordination mode with S–metal interaction,[14] whereas this double bridging co-ordination is very rare among bridging aminocarbene complexes.[15]

Molecular structure of $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)\{C(O)Bu^n\}(Cp)_2]$ 4b

The molecular structure of **4b** is reported in Fig. 1 and bond lengths and angles in Table 1. Its stereogeometry is consistent with that of the cation of **2a**. The inner diamond Fe_2C_2 is bent around the Fe–Fe bond [2.504(1) Å long] with a dihedral angle of 23.4(1)°. An effect of the attack of the Bu^n group at one of the terminal CO ligands is the loss of the C_s symmetry of the parent cation and the formation of crystals containing a racemic mixture of asymmetric molecules. The bond parameters in this molecule are strictly equivalent to those found in $[Fe_2\{\mu\text{-}CN(Me)CH_2Ph\}(\mu\text{-}CO)(CO)\{C(O)C_4H_3S\}(Cp)_2]$,[6] obtained by reaction of a type **2** cation with thienyllithium. Therefore the rationalization of the electronic structure given for the latter species applies to the present one, *i.e.* the acyl ligand acts as a two-electron anionic ligand and the bridging CNMe₂ group as a two-electron donor iminium cation. The slight asymmetry of the μ-CNMe₂ ligand [C(4)–Fe(1) 1.843(3), C(4)–Fe(2) 1.877(3) Å] and the strong asymmetry of the μ-CO ligand [C(3)–Fe(1) 1.843(3), C(3)–Fe(2) 2.002(3) Å] are explained by an increased back donation from the more electron rich Fe(1) atom.

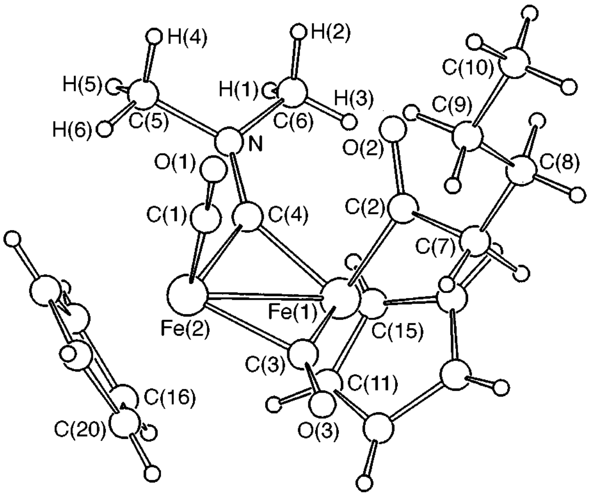


Fig. 1 Molecular structure of $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)\{C(O)Bu^n\}(Cp)_2]$ **4b**

Table 1 Bond lengths (Å) and angles (°) for $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)\{C(O)Bu^n\}(Cp)_2]$ **4b**

Fe(2)–Fe(1)	2.504(1)	C(2)–O(2)	1.199(4)
Fe(1)–C(4)	1.843(3)	C(2)–C(7)	1.534(5)
Fe(2)–C(4)	1.877(3)	C(7)–C(8)	1.515(5)
C(4)–N	1.296(4)	C(8)–C(9)	1.462(7)
N–C(6)	1.463(5)	C(9)–C(10)	1.531(7)
N–C(5)	1.474(5)	Fe(2)–C(1)	1.751(4)
Fe(1)–C(3)	1.843(3)	C(1)–O(1)	1.138(4)
Fe(2)–C(3)	2.002(3)	Fe(1)–C(Cp_{ave})	2.143(2)
C(3)–O(3)	1.178(4)	Fe(2)–C(Cp_{ave})	2.122(3)
Fe(1)–C(2)	1.972(3)		
N–C(4)–Fe(1)	140.0(3)	O(1)–C(1)–Fe(2)	177.0(3)
N–C(4)–Fe(2)	135.4(2)	C(1)–Fe(2)–C(4)	89.4(2)
C(6)–N–C(5)	113.3(3)	C(4)–Fe(1)–C(2)	87.45(13)
C(4)–N–C(5)	123.2(3)	C(7)–C(2)–Fe(1)	118.4(2)
C(4)–N–C(6)	123.5(3)	O(2)–C(2)–Fe(1)	124.9(3)
O(3)–C(3)–Fe(1)	145.9(3)	O(2)–C(2)–C(7)	116.6(3)
O(3)–C(3)–Fe(2)	132.7(3)		

Another feature to be commented upon is that the acyl ligands $C(O)Bu^n$ and C(O)th in the respective molecules have the same orientation around the Fe–C axis with the acyl oxygen pointing towards the iminium ligand. This may indicate that the preferred direction of CO attack by the carbanions is from the less hindered side opposite to the iminium grouping and/or the presence of stabilizing interligand interactions involving the acyl oxygen [O(2)]. An analysis of the non-bonded contacts shows the following distances of atoms in the iminium ligand from O(2): N 3.01, C(4) 2.79, C(5) 4.07, C(6) 3.04, H(2) 3.02, H(3) 2.65 Å, some of these values being shorter than the sum of the van der Waals radii.[16] In addition a comparison of the C(4)–Fe–C angles formed by the C(1) (carbonyl) and C(2) (acyl) atoms [89.4, 87.4(2)°, respectively] indicates that the interactions between O(2) and the iminium atoms are at least not repulsive, otherwise the C(4)–Fe(1)–C(2) angle would have been found to be the wider one.

An extended-Hückel calculation of the charge distribution in the molecule (Table 2) shows, as expected, negative charges localized on the three oxygen atoms with the most negative value on O(2). On the contrary the positive charges are distributed on the iron atoms, and on the carbons connected to both

Table 2 Charges (eV) at relevant atoms in molecule **4b** obtained by extended-Hückel calculations

Fe(1)	+0.224	C(4)	+0.036
Fe(2)	+0.201	C(5,6)	+0.085
C(1)	+0.087	N	−0.055
O(1)	−0.263	H(1)–H(6)	+0.026
C(2)	+0.038	C(11)–C(15)	−0.014
O(2)	−0.373	H(11)–H(15)	+0.005
C(3)	+0.051	C(16)–C(20)	+0.003
O(3)	−0.335	H(16)–H(20)	+0.001

oxygen and nitrogen atoms. It is noteworthy that the C(6) and C(4) atoms (+0.085, +0.036 eV, respectively) are at a distance less than the van der Waals radii sum from the acyl oxygen [O(2), −0.373 eV]. This situation indicates a favourable inter-ligand electrostatic interaction.

The Fe(1)–C(2) (acyl) bond length [1.972(3) Å] can be compared to the few analogous values reported so far: 1.964(4) Å in [Fe$_2${μ-CN(Me)CH$_2$Ph}(μ-CO)(CO){C(O)th}(Cp)$_2$][6] 1.992(8) Å in [Fe(CO){C(O)Bu^n}(Cp)(PPh$_3$)],[17] 1.976(6) Å in [Fe(CO)(CH$_3$CO)(Cp){Ph$_2$PNHCH(Me)(Ph)}].[18]

Experimental

All the reactions were routinely carried out under nitrogen by standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Glassware was oven-dried before use. Infrared spectra were recorded on a Perkin-Elmer 983-G spectrophotometer, ^{1}H and ^{13}C NMR spectra on a Varian Gemini 200. The shiftless relaxation reagent [Cr(acac)$_3$] (acac = acetylacetonate) was added to solutions studied by ^{13}C NMR spectroscopy. Elemental analyses were performed by Pascher Microanalytical Laboratory (Remagen, Germany). All the reagents were commercial products (Aldrich) of the highest purity available and used as received; [Fe$_2$(CO)$_4$(Cp)$_2$] was from Strem. Compounds [Fe$_2$(μ-CNMe$_2$)(μ-CO)(CO)$_2$(Cp)$_2$]SO$_3$CF$_3$ **2a**[7] and [Fe$_2${μ-CN(Me)CH$_2$Ph}(μ-CO)(CO)$_2$(Cp)$_2$]SO$_3$CF$_3$ **2b**[8] were synthesized according to published methods. The species Li$_2$Cu(CN)R′$_2$ were prepared from CuCN and the appropriate organolithium reagent according to the literature.[19]

Syntheses

[Fe$_2$(μ-CNMe$_2$)(μ-CO)(CO)$_2$(C$_5$H$_5$Me)(Cp)] 3a. *Method a.* Methyllithium (0.34 cm^3 of a solution 1.5 M in Et$_2$O) was added to a stirred solution of **2a** (0.25 g, 0.47 mmol) in thf (15 cm^3) at −40 °C. The solution was then warmed to room temperature, stirred for an additional 30 min and filtered on a Celite pad. Removal of the solvent and chromatography on an alumina column, with CH$_2$Cl$_2$–hexane mixture (1 : 2 v/v) as eluent, gave a green band, which afforded dark green crystals of **3a** (0.16 g, 87%) (Found: C, 51.1; H, 5.0. C$_{17}$H$_{19}$Fe$_2$NO$_3$ requires C, 51.4; H, 4.8%); ν$_{max}$/cm^{-1} (CH$_2$Cl$_2$) 1959vs, 1921m and 1771s (CO) and 1561mw (C=N); δ$_H$(CDCl$_3$) 4.66 (5 H, s, Cp), 4.61, 4.22, 3.51, 3.43, 3.18 (5 H, m, C$_5$*H*$_5$Me), 3.91 (3 H, s, NMe), 3.79 (3 H, s, NMe) and 0.47 [d, *J*(HH) 6.2 Hz, C$_5$H$_5$*Me*]; δ$_C$(CD$_2$Cl$_2$) 330.0 (μ-*C*NMe$_2$), 266.9 (μ-CO), 222.9, 214.3 (CO), 85.3 (Cp), 88.2, 84.6, 84.4, 70.3, 70.1 (*C*$_5$H$_5$Me), 52.4, 52.1 (NMe) and 29.6 (C$_5$H$_5$*Me*).

[Fe$_2$(μ-CNMe$_2$)(μ-CO)(CO)$_2$(C$_5$H$_5$Bu^n)(Cp)] 3b. Compound **3b** was prepared as described for the synthesis of **3a** by treating **2a** (0.265 g, 0.50 mmol) with LiBu^n (0.31 cm^3 of a 1.6 M solution in hexane). Yield 0.17 g, 78% (Found: C, 54.6; H, 5.7. C$_{20}$H$_{25}$Fe$_2$NO$_3$ requires C, 54.7; H, 5.7%); ν$_{max}$/cm^{-1} (CH$_2$Cl$_2$) 1958vs, 1920m and 1770s (CO) and 1561mw (C=N); δ$_H$(CDCl$_3$) 4.66 (5 H, s, Cp), 4.60, 4.24, 3.52, 3.35, 3.20 (5 H, m, C$_5$*H*$_5$Me), 3.90 (3 H, s, NMe), 3.77 (3 H, s, NMe), 1.13–0.68 (9 H, m, C$_5$H$_5$*Bu*^{n}); δ$_C$(CD$_2$Cl$_2$) 330.0 (μ-*C*NMe$_2$), 267.2 (μ-CO), 222.9, 214.2 (CO), 85.4 (Cp), 88.9, 85.1, 68.8, 68.7, 58.1 (*C*$_5$H$_5$Me), 52.2, 52.1 (NMe), 44.1, 29.1, 23.2 and 14.2 (C$_5$H$_5$*Bu*^{n}).

[Fe$_2$(μ-CNMe$_2$)(μ-CO)(CO)$_2$(C$_5$H$_5$Ph)(Cp)] 3c. Compound **3c** was prepared as described for the synthesis of **3a** by treating **2a** (0.238 g, 0.45 mmol) with LiPh (0.25 cm^3 of a 1.8 M solution in hexane). Yield 0.17 g, 83% (Found: C, 57.5; H, 4.7. C$_{22}$H$_{21}$Fe$_2$NO$_3$ requires C, 57.6; H, 4.6%); ν$_{max}$/cm^{-1} (CH$_2$Cl$_2$) 1962vs, 1925m and 1774s (CO) and 1561mw (C=N); δ$_H$(CDCl$_3$) 7.2–6.9 (5 H, m, C$_5$H$_5$*Ph*), 4.70 (5 H, s, Cp), 4.69, 4.60, 4.34, 3.61, 3.39 (5 H, m, C$_5$*H*$_5$Ph), 3.90 (3 H, s, NMe), 3.80 (3 H, s, NMe); δ$_C$(CD$_2$Cl$_2$) 330.1 (μ-*C*NMe$_2$), 267.1 (μ-CO), 222.5, 214.4 (CO), 149.2, 128.8, 126.6, 126.3 (C$_5$H$_5$*Ph*), 85.9 (Cp), 89.3, 85.2, 67.7, 67.5, 61.5 (*C*$_5$H$_5$Ph), 52.7 and 52.6 (NMe).

[Fe$_2${μ-CN(Me)CH$_2$Ph}(μ-CO)(CO)$_2$(C$_5$H$_5$Me)(Cp)] 3d. The procedure was the same as that used for the preparation of compound **3a** except that **2b** (0.32 g, 0.55 mmol) was used instead of **2a** yielding **3d** (0.21 g, 82%) (Found: C, 58.4; H, 4.9. C$_{23}$H$_{23}$Fe$_2$NO$_3$ requires C, 58.4; H, 4.9%); ν$_{max}$/cm^{-1} (CH$_2$Cl$_2$) 1960vs, 1925m and 1788s (CO) and 1518mw (C=N); δ$_H$(CDCl$_3$) (α isomer) 7.52–7.24 (5 H, m, Ph), 5.49 [1 H, d, *J*(AB) 14, C*H*$_2$Ph], 5.22 [1 H, d, *J*(AB) 14, C*H*$_2$Ph], 4.73 (5 H, s, Cp), 4.67, 4.30, 3.53, 3.43, 3.00 (5 H, m, C$_5$*H*$_5$Me), 3.74 (3 H, s, NMe) and 0.42 [3 H, d, *J*(HH) 6 Hz, C$_5$H$_5$*Me*]; (β isomer) 7.52–7.24 (5 H, m, Ph), 5.67 [1 H, d, *J*(AB) 15, C*H*$_2$Ph], 5.43 [1 H, d, *J*(AB) 15, C*H*$_2$Ph], 4.64 (5 H, s, Cp), 4.67, 4.38, 3.53, 3.43, 3.25 (5 H, m, C$_5$*H*$_5$Me), 3.64 (3 H, s, NMe) and 0.50 [3 H, d, *J*(HH) 6 Hz, C$_5$H$_5$*Me*]; α : β isomers ratio ≈ 2.2 : 1; δ$_C$(CD$_2$Cl$_2$) (α isomer) 333.1 (μ-*C*NMe$_2$), 266.9 (μ-CO), 223.3, 214.6 (CO), 136.9, 129.8, 128.7, 127.7 (Ph), 85.9 (Cp), 88.9, 85.2, 71.0, 70.5 (*C*$_5$H$_5$Me), 52.7 (N*C*H$_2$Ph), 49.8 (NMe) and 29.4 (C$_5$H$_5$*Me*); (β isomer) 333.8 (μ-*C*NMe$_2$), 266.3 (μ-CO), 223.3, 214.9 (CO), 136.5, 129.8, 128.7, 127.7 (Ph), 85.8 (Cp), 88.9, 85.2, 71.1, 70.3 (*C*$_5$H$_5$Me), 52.9 (N*C*H$_2$Ph), 49.9 (NMe) and 29.6 (C$_5$H$_5$*Me*).

[Fe$_2${μ-CN(Me)CH$_2$Ph}(μ-CO)(CO)$_2$(C$_5$H$_5$Bu^n)(Cp)] 3e. The procedure was the same as that used for the preparation of compound **3b** except that **2b** (0.28 g, 0.48 mmol) was used instead of **2a** yielding **3e** (0.17 g, 68%) (Found: C, 60.5; H, 5.8. C$_{26}$H$_{29}$Fe$_2$NO$_3$ requires C, 60.6; H, 5.7%); ν$_{max}$/cm^{-1} (CH$_2$Cl$_2$) 1957vs, 1926m and 1786s (CO) and 1519mw (C=N); δ$_H$(CDCl$_3$) (α isomer) 7.50–7.18 (5 H, m, Ph), 5.43 [1 H, d, *J*(AB) 15, C*H*$_2$Ph], 5.24 [1 H, d, *J*(AB) 15 Hz, C*H*$_2$Ph], 4.73 (5 H, s, Cp), 4.67, 4.30, 3.54, 3.31, 3.02 (5 H, m, C$_5$*H*$_5$Bu^n), 3.71 (3 H, s, NMe), 1.2–0.5 (9 H, m, Bu^n); (β isomer) 7.50–7.18 (5 H, m, Ph), 5.68 [1 H, d, *J*(AB) 15, C*H*$_2$Ph], 5.44 [1 H, d, *J*(AB) 15 Hz, C*H*$_2$Ph], 4.65 (5 H, s, Cp), 4.67, 4.38, 3.54, 3.31, 3.02 (5 H, m, C$_5$*H*$_5$Bu^n), 3.62 (3 H, s, NMe) and 1.2–0.5 (9 H, m, Bu^n); α : β isomers ratio ≈ 2.5 : 1.

[Fe$_2${μ-CN(Me)CH$_2$Ph}(μ-CO)(CO)$_2$(C$_5$H$_5$Ph)(Cp)] 3f. The procedure was the same as that used for the preparation of compound **3c** except that **2b** (0.26 g, 0.45 mmol) was used instead of **2a** yielding **3f** (0.15 g, 61%) (Found: C, 62.5; H, 4.7. C$_{28}$H$_{25}$Fe$_2$NO$_3$ requires C, 62.8; H, 4.7%); ν$_{max}$/cm^{-1} (CH$_2$Cl$_2$) 1965vs, 1928m and 1776s (CO) and 1520mw (C=N); δ$_H$(CDCl$_3$) (α isomer) 7.50–6.90 (10 H, m, Ph), 5.53 [1 H, d, *J*(AB) 15, C*H*$_2$Ph], 5.27 [1 H, d, *J*(AB) 15 Hz, C*H*$_2$Ph], 4.74 (5 H, s, Cp), 4.60, 4.37, 3.45, 3.21 (5 H, m, C$_5$*H*$_5$Me) and 3.74; (β isomer) 7.50–6.90 (10 H, m, Ph), 5.67 [1 H, d, *J*(AB) 15, C*H*$_2$Ph], 5.43 [1 H, d, *J*(AB) 15 Hz, C*H*$_2$Ph], 4.66 (5 H, s, Cp), 4.60, 4.42, 3.45, 3.21 (5 H, m, C$_5$*H*$_5$Me) and 3.68 (3 H, s, NMe); α : β isomers ratio ≈ 2.6 : 1.

[Fe$_2$(μ-CNMe$_2$)(μ-CO)(CO)$_2$(C$_5$H$_5$Me)(Cp)] 3a. *Method b.* Complex **2a** (0.18 g, 0.34 mmol) was treated with a slight excess of MeMgCl (0.36 mmol) in thf (20 cm^3) at 0 °C. The mixture was then stirred at room temperature for about 30 min and filtered on an alumina pad. Removal of the solvent under reduced pressure and chromatography on an alumina column with a CH_2Cl_2–hexane mixture (1:3 v/v) as eluent afforded a brownish green fraction of **3a** (67 mg, 50%).

[Fe$_2$(μ-CNMe$_2$)(μ-CO)(CO)$_2${C$_5$H$_5$(CH$_2$Ph)}(Cp)] 3g. Freshly prepared PhCH$_2$MgCl (0.30 mmol) in thf solution (10 cm^3) was added to a solution of **2a** (0.14 g, 0.27 mmol) in thf (15 cm^3) at 0 °C. Work-up of the reaction mixture as described for the synthesis of **3a** (method b) yielded **3g** (55 mg, 43%) (Found: C, 58.3; H, 4.9. $C_{23}H_{23}Fe_2NO_3$ requires C, 58.4; H, 4.9%); ν_{max}/cm^{-1} (CH_2Cl_2) 1961vs, 1923m and 1774s (CO), 1561mw and 1537mw (C=N); δ_H($CDCl_3$) 7.30–6.90 (5 H, m, Ph), 4.59 (5 H, s, Cp), 4.20, 3.51, 3.42, 3.08 (5 H, m, C$_5$*H*$_5$CH$_2$Ph), 3.81 (3 H, s, NMe), 3.65 (3 H, s, NMe) and 1.98 (2 H, m, C*H*$_2$Ph); δ_C(CD_2Cl_2) 329.8 (μ-*C*NMe$_2$), 267.1 (μ-CO), 222.7, 214.3 (CO), 140.5, 129.4, 128.6, 125.9 (C$_5$H$_5$CH$_2$*Ph*), 85.7 (Cp), 88.8, 85.1, 67.9, 67.8, 59.3 (*C*$_5$H$_5$CH$_2$Ph), 52.4, 53.2 (NMe) and 51.0 (C$_5$H$_5$*C*H$_2$Ph).

[Fe$_2$(μ-CNMe$_2$)(μ-CO)(CO)$_2$(C$_5$H$_5$Pr^i)(Cp)] 3h. Compound **3h** was prepared as described for **3g** by treating **2a** (0.24 g, 0.45 mmol) with freshly prepared Pr^{i}MgCl (0.48 mmol). Yield 96 mg, 47% (Found: C, 54.0; H, 5.5. $C_{19}H_{23}Fe_2NO_3$ requires C, 53.7; H, 5.4%); ν_{max}/cm^{-1} (CH_2Cl_2) 1958vs, 1920m and 1770s (CO), 1555mw and 1537mw (C=N); δ_H($CDCl_3$) 4.67 (5 H, s, Cp), 4.60, 4.28, 3.49, 3.30, 3.04 (5 H, m, C$_5$*H*$_5$Pr^i), 3.89 (3 H, s, NMe), 3.76 (3 H, s, NMe) and 0.68 (6 H, m, Pr^i); δ_C(CD_2Cl_2) 330.3 (μ-*C*NMe$_2$), 267.8 (μ-CO), 223.0, 214.6 (CO), 85.8 (Cp), 89.2, 85.5, 67.5, 67.3, 65.7 (*C*$_5$H$_5$Pr^i), 52.5, 52.4 (NMe), 41.3 and 19.8 (C$_5$H$_5$*Pr*^{i}).

[Fe$_2${μ-CN(Me)CH$_2$Ph}(μ-CO)(CO)$_2${C$_5$H$_5$(CH$_2$Ph)}(Cp)] 3i. The complex **3i** was prepared as described for the synthesis of **3g** by treating **2b** (0.35 g, 0.60 mmol) with an equimolar amount of freshly prepared PhCH$_2$MgCl. Yield 0.15 g, 45% (Found: C, 63.4; H, 5.0. $C_{29}H_{27}Fe_2NO_3$ requires C, 63.4; H, 4.9%); ν_{max}/cm^{-1} (CH_2Cl_2) 1959vs, 1927m and 1786s (CO) and 1518mw (C=N); δ_H($CDCl_3$) (α isomer) 7.50–6.90 (10 H, m, Ph), 5.35 [1 H, d, *J*(AB) 15, NC*H*$_2$Ph], 5.21 [1 H, d, *J*(AB) 15 Hz, NC*H*$_2$Ph], 4.71 (5 H, s, Cp), 4.68, 4.32, 3.73, 3.52, 3.08 (5 H, m, C$_5$*H*$_5$CH$_2$Ph), 3.71 (3 H, s, NMe) and 1.96 (2 H, m, C*H*$_2$Ph); (β isomer) 7.50–6.90 (10 H, m, Ph), 5.65 [1 H, d, *J*(AB) 15, NC*H*$_2$Ph], 5.39 [1 H, d, *J*(AB) 15 Hz, NC*H*$_2$Ph], 4.63 (5 H, s, Cp), 4.68, 4.38, 3.73, 3.52, 3.22 (5 H, m, C$_5$*H*$_5$CH$_2$Ph), 3.57 (3 H, s, NMe) and 1.96 (2 H, m, C*H*$_2$Ph); α:β isomers ratio ≈ 2.2:1.

[Fe$_2$(μ-CNMe$_2$)(μ-CO)(CO){C(O)Me}(Cp)$_2$] 4a. Compound **2a** (0.21 g, 0.40 mmol) in thf (15 cm^3) at −40 °C was treated with a solution of Li$_2$Cu(CN)Me$_2$ prepared from dry CuCN (45 mg, 0.5 mmol) and LiMe (1.1 mmol) in thf (10 cm^3) at −80 °C. The mixture was then warmed to room temperature and stirred for an additional 30 min. Filtration on a Celite pad and removal of the solvent gave a brown residue that was chromatographed on an alumina column with a CH_2Cl_2–hexane mixture (1:1 v/v) as eluent. A green band was collected and afforded dark green crystals of **4a** (0.11 g, 71%) (Found: C, 51.2; H, 4.8. $C_{17}H_{19}Fe_2NO_3$ requires C, 51.4; H, 4.8%); ν_{max}/cm^{-1} (CH_2Cl_2) 1963vs, 1773s and 1601m (CO) and 1549mw (C=N); δ_H($CDCl_3$) 4.71 (10 H, s, Cp), 4.04 (3 H, s, Me), 4.00 (3 H, s, Me) and 2.08 (3 H, s, COMe); δ_C(CD_2Cl_2) 331.0 (μ-*C*NMe$_2$), 269.3, 268.0 (μ-CO and *C*OMe), 215.1 (CO), 89.1, 86.8 (Cp), 52.6, 51.4 (NMe$_2$) and 46.4 (CO*Me*).

[Fe$_2$(μ-CNMe$_2$)(μ-CO)(CO){C(O)Bu^n}(Cp)$_2$] 4b. The complex **4b** was prepared as described for the synthesis of **4a** by reacting **2a** (0.30 g, 0.56 mmol) with a slight excess of Li$_2$Cu(CN)Bu$_2$. Yield 0.18 g, 75% (Found: C, 54.8; H, 5.7. $C_{20}H_{25}Fe_2NO_3$ requires C, 54.7; H, 5.7%); ν_{max}/cm^{-1} (CH_2Cl_2) 1958vs, 1771s and 1599m (CO) and 1544mw (C=N); δ_H($CDCl_3$) 4.62 (10 H, s, Cp), 4.06 (3 H, s, NMe), 3.99 (3 H, s, NMe), 2.78–2.48 [2 H, m, C*H*$_2$(CH$_2$)$_2$CH$_3$], 0.96 [4 H, m, CH$_2$(C*H*$_2$)$_2$CH$_3$] and 0.68 [3 H, m, CH$_2$(CH$_2$)$_2$C*H*$_3$]; δ_C(CD_2Cl_2) 330.9 (μ-*C*NMe$_2$), 269.3, 269.2 (μ-CO and *C*OBu^n), 215.0 (CO), 88.9, 86.7 (Cp), 59.7, 28.1, 22.8, 14.4 (Bu^n), 52.5 and 51.2 (NMe).

[Fe$_2${μ-CN(Me)CH$_2$Ph}(μ-CO)(CO){C(O)Bu^n}(Cp)$_2$] 4c. Compound **4c** was prepared following the same procedure described for the synthesis of **4b** except that **2b** (0.28 g, 0.48 mmol) was used instead of **2a**. Yield 0.19 g, 77% (Found: C, 60.6; H, 5.6. $C_{26}H_{29}Fe_2NO_3$ requires C, 60.6; H, 5.7%); ν_{max}/cm^{-1} (CH_2Cl_2) 1959vs, 1777s and 1610m (CO) and 1524mw (C=N); δ_H($CDCl_3$) (α isomer) 7.50–7.36 (5 H, m, Ph), 5.82 [1 H, d, *J*(AB) 15, C*H*$_2$Ph], 5.51 [1 H, d, *J*(AB) 15 Hz, C*H*$_2$Ph], 4.77 (5 H, s, Cp), 4.67 (5 H, s, Cp), 3.99 (2 H, s, NMe), 2.91–2.50 [2 H, m, C*H*$_2$(CH$_2$)$_2$CH$_3$], 1.08 [4 H, m, CH$_2$(C*H*$_2$)$_2$CH$_3$] and 0.76 [3 H, m, CH$_2$(CH$_2$)$_2$C*H*$_3$]; (β isomer) 7.50–7.36 (5 H, m, Ph), 6.19 [1 H, d, *J*(AB) 16, C*H*$_2$Ph], 5.41 [1 H, d, *J*(AB) 16 Hz, C*H*$_2$Ph], 4.77 (5 H, s, Cp), 4.62 (5 H, s, Cp), 3.92 (3 H, s, NMe), 2.91–2.50 [2 H, m, C*H*$_2$(CH$_2$)$_2$CH$_3$], 1.08 [4 H, m, CH$_2$(C*H*$_2$)$_2$CH$_3$] and 0.76 [3 H, m, CH$_2$(CH$_2$)$_2$C*H*$_3$]; α:β isomers ratio = 0.9:1; δ_C(CD_3CN) (α + β isomers) 334.6, 333.9 (μ-*C*NMe$_2$), 269.4, 269.1, 268.6, 268.0 (μ-CO and *C*OBu^n), 215.3, 214.9 (CO), 137.8–127.6 (Ph), 89.2, 87.0, 86.9 (Cp), 70.5, 68.9 (N*C*H$_2$Ph), 60.1, 59.9, 28.3, 28.2, 22.9, 14.4 (Bu^n), 50.3 and 48.5 (NMe).

[Fe$_2$(μ-CNMe$_2$)(μ-CO)(CO){C(O)C≡CPh}(Cp)$_2$] 5a. To a stirred solution of **2a** (0.22 g, 0.41 mmol) in thf (15 cm^3) at −20 °C was added a slight excess of LiC≡CPh (0.45 mmol) freshly prepared from PhC≡CH and BuLi. The mixture was stirred for 60 min, warmed to room temperature and then filtered on a Celite pad. Removal of the solvent and chromatography of the residue on an alumina column with a CH_2Cl_2–hexane mixture (1:1 v/v) as eluent gave a greenish brown fraction which was collected. Crystallization from CH_2Cl_2 layered with pentane at −20 °C yielded **5a** (0.11 g, 56%) (Found: C, 59.8; H, 4.7. $C_{24}H_{21}Fe_2NO_3$ requires C, 59.7; H, 4.4%); ν_{max}/cm^{-1} (CH_2Cl_2) 1969vs, 1790s and 1573m (CO), 1550mw (C=N) and 2161w (C≡C); δ_H($CDCl_3$) 7.55–7.29 (5 H, m, Ph), 4.86 (5 H, s, Cp), 4.76 (5 H, s, Cp), 4.10 (3 H, s, NMe) and 4.06 (3 H, s, NMe); δ_C($CDCl_3$) 331.3 (μ-*C*NMe$_2$), 266.2 (μ-CO), 251.8 (*C*OC≡), 214.8 (CO), 132.5, 129.4, 129.0, 123.5 (Ph), 90.8, 87.0 (Cp), 91.7, 88.2 (C≡C), 52.8 and 51.5 (NMe$_2$).

[Fe$_2$(μ-CNMe$_2$)(μ-CO)(CO){C(O)C≡CC$_6$H$_4$Me-4}(Cp)$_2$] 5b. Compound **5b** was obtained as described for the synthesis of **5a** starting from **2a** (0.26 g, 0.48 mmol) and LiC≡CC$_6$H$_4$Me-4, freshly generated from 4-ethynyltoluene and BuLi. Yield 0.11 g, 48% (Found: C, 57.0; H, 4.9. $C_{22}H_{23}Fe_2NO_3$ requires C, 57.3; H, 5.0%); ν_{max}/cm^{-1} (CH_2Cl_2) 1968vs, 1790s and 1606m (CO), 1571m (C=N) and 2163w (C≡C); δ_H($CDCl_3$) 7.42–7.15 (4 H, m, Ph), 4.86 (5 H, s, Cp), 4.77 (5 H, s, Cp), 4.11 (3 H, s, NMe), 4.06 (3 H, s, NMe) and 2.36 (3 H, s, C$_6$H$_4$*Me*); δ_C($CDCl_3$) 330.7 (μ-*C*NMe$_2$), 267.0 (μ-CO), 251.6 (*C*OC≡), 214.8 (CO), 139.9, 132.5, 129.8, 120.3 (*C*$_6$H$_4$Me), 90.7, 87.0 (Cp), 91.5, 86.9 (C≡C), 52.8, 51.4 (NMe$_2$) and 21.9 (C$_6$H$_4$*Me*).

Crystallography

Crystal data and details of the data collection for [Fe$_2$(μ-CNMe$_2$)(μ-CO)(CO){C(O)Bu^n}(Cp)$_2$] **4b** are given in Table 3. The diffraction experiments were carried out at room temperature on a fully automated Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-Kα radiation. The unit-cell parameters were determined by a least-squares fitting procedure using 25 reflections. Data were corrected for Lorentz and polarization effects. No decay correction was necessary. An empirical absorption correction was applied by using the azimuthal scan method.[20] The positions of the metal atoms

Table 3 Crystal data and experimental details for [Fe_2(μ-$CNMe_2$)-(μ-CO)(CO){C(O)Bu^n}$(Cp)_2$] **4b**

Formula	$C_{20}H_{25}Fe_2NO_3$
M	439.11
T/K	293(2)
λ/Å	0.710 69
Crystal symmetry	Monoclinic
Space group	$P2_1/n$ (no. 14)
a/Å	9.368(5)
b/Å	15.881(4)
c/Å	13.251(3)
β/°	98.18(3)
U/Å^3	1951(1)
Z	4
D_c/Mg m^{-3}	1.495
μ(Mo-Kα)/mm^{-1}	1.505
F(000)	912
Crystal size/mm	0.08 × 0.15 × 0.4
θ Limits/°	2–30
Scan mode	ω
Absorption correction	Empirical *via* ψ scans
Maximum, minimum transmission factors	0.990, 0.730
Reflections collected	6335 ($\pm h$, $+k$, $\pm l$)
Unique observed reflections [$F_o > 4\sigma(F_o)$], parameters (R_{int})	3503, 220 (0.013)
Goodness of fit on F^2	1.052
$R1$ (F),[a] $wR2$ (F^2)[b]	0.0413, 0.1104
Weighting scheme a, b	0.0688, 1.3589[b]
Largest difference peak, hole/e Å^{-3}	0.878, −0.54

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

were found by direct methods using the SHELXS 86 program[21] and all the non-hydrogen atoms located from Fourier-difference syntheses. The hydrogen atoms of the methyl group were located from successive Fourier-difference maps and a constraint of equal C–H bonds was applied. The cyclopentadienyl hydrogen atoms were added in calculated positions. The final refinement on F^2 proceeded by full-matrix least-squares calculations (SHELXL 93)[22] using anisotropic thermal parameters for all the non-hydrogen atoms. The methyl and methylene H atoms were assigned an isotropic thermal parameter 1.2 times U_{eq} of the carbon atoms to which they were attached. In the final Fourier-difference synthesis the electron density was found in the range −0.54 to 0.88 e Å^{-3}.

CCDC reference number 186/758.

Extended-Hückel molecular orbital calculations[23] were carried out on the experimental structure using the modified Wolfberg–Helmholz formula.[24] Standard atomic parameters were used for C, O, N and H, while that for Fe was taken from the literature.[25] A self-consistent charge calculation was performed assuming a quadratic dependence of H_{ii} on charge.

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