Preparation and Properties of Carbonyliron Complexes of 1-Aza-4-oxa-1,3-butadiene (α-Imino Ketone) – X-ray Crystal Structures of $Fe(CO)_3[MeN{=}C(Ph)C(Ph){=}O]$ and $Fe_2(CO)_4[tBuN{=}C(H)(Me)C(O)(O)C(Me)C(H){=}NtBu]$

Ron Siebenlist,[a] Hans-Werner Frühauf,*[a] Kees Vrieze,[a] Wilberth J. J. Smeets,[b] and Anthony L. Spek[b]

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The reaction of $Fe_2(CO)_9$ at room temperature in THF or toluene with the α-imino ketones $R^1N{=}C(R^2)–C(R^3){=}O$ (L) (R^1 = alkyl, R^2 = H, Me, Ph, R^3 = Me, Ph) (**a–k**), initially results in the formation of the mononuclear chelate $Fe(CO)_3$(α-imino ketone) complexes **6** which can be isolated in moderate (**6h**) to high (**6e–g**) yield. Under these reaction conditions, complexes **6** subsequently react with $[Fe(CO)_4]$ fragments or dimerise, to form the dinuclear complexes $Fe_2(CO)_6$(α-imino ketone) (**7a–j**) or $Fe_2(CO)_4$(L–L) (**8a,b,k**), respectively. The complexes **8** contain two α-imino ketone ligands C–C coupled at the ketone carbon atoms. Complexes **8a,b** react with CO at elevated temperatures to quantitatively yield $Fe(CO)_3$(α-imino ketone) (**6a,b**). This reaction can be reversed photochemically. Irradiation of a solution of **6a,b** in the low-energy band results in the reformation of **8a,b** in almost quantitative yield. The extremely air-sensitive complexes **6** and the dinuclear complexes **7** and **8** have been characterised spectroscopically (IR, UV/Vis, ^1H and ^{13}C NMR) and by elemental analysis. The solid state structures of complexes **6g** and **8a** have been determined by single-crystal X-ray diffraction. The molecular structure of **6g** confirms the flat σ-*O*,σ-*N* chelate coordination of the α-imino ketone. The structure of **8a** consists of two metal–metal-bonded $Fe(CO)_2$ units, bridged by a formally 10e-donating dianionic C–C coupled (*t*Bu-ADO) ligand. A mechanism for the formation of complexes **8** is discussed.

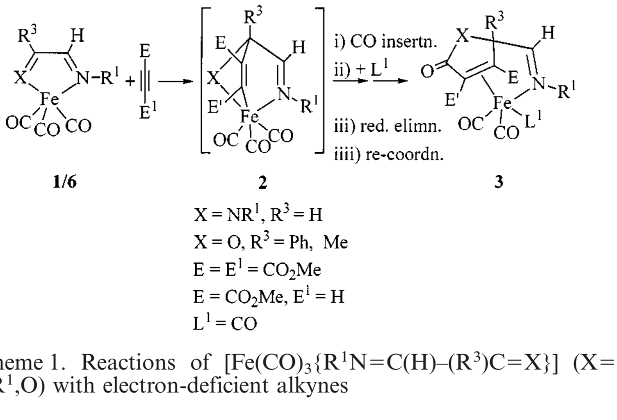
Introduction

The reaction of α-diimine ligands $R^1N{=}C(H)–C(H){=}NR^1$ (R-DAB) (cf. Table 1) and C_5H_4N-2-$C(H){=}NR^1$ (R-Pyca) (cf. Table 1) with carbonylmetal compounds of the iron triad leads to the formation of several mono-, di-, and polynuclear complexes.[1–5] The ability to donate the nitrogen lone pairs and the (C=N) imine π-bonds results in a flexible coordination behaviour in which the α-diimine ligand can donate from 2 to 8 electrons to one or more metal centres. An interesting aspect of this versatile coordination behaviour is the activation of the imine bond towards C–C, C–H, C–N, and N–H coupling reactions of R-DAB ligands in the coordination sphere of transition metals with a variety of unsaturated molecules, such as α-diimines[6–10] carbodiimides[11] sulfines,[11] and alkynes.[12–18]

Table 1. Abbreviations used throughout this text

Abbreviation	Explanation
R-DAB	1,4-Diaza-1,3-butadienes of formula $R^1N{=}C(H)–C(H){=}NR^1$
R-Pyca	1,4-Diaza-1,3-dienes of formula C_5H_4N-2-$C(H){=}NR^1$
DMAD	Dimethyl acetylenedicarboxylate
MP	Methyl propynoate
*t*Am	2-Methyl-2-butyl
R-ADO	1,6-Di-R-1,6-diazahexa-1,5-diene-3,4-dimethyl-3,4-diolato, $R^1N{=}C(H)(Me)C(O)HC(O)C(Me){=}NR^1$
OPB	2,3-Diolato-2,3-bis(2-pyridyl)butane, $[C_5H_4N\text{-}2]CMe(O)CMe(O)[2\text{-}C_5H_4N]$
R-ADA	1,6-Di-R-1,6-diazahexa-1,5-diene-3,4-di-R-aminato, the reductively C–C coupled dimer of R-DAB; $R^1N{=}C(H)(H)C(NR^1)(H)C(NR^1)C(H){=}NR^1$
R-APE	1,2-Di-R-aminato-1,2-bis(2-pyridyl)ethane, the reductively C–C coupled dimer of R-Pyca; $[C_5H_4N\text{-}2]CH(NR^1)CH(NR^1)[2\text{-}C_5H_4N]$

In a series of previous papers[19–24] we have reported in detail on the C–C coupling reaction of the $[(R\text{-}DAB)Fe(CO)_3]$ complexes **1** (cf. Scheme 1; X = NR^1, R^3 = H) with the electron-deficient alkynes dimethyl acetylenedicarboxylate (DMAD) (cf. Table 1) and methyl propynoate (MP) (cf. Table 1). The initial step in this reaction can be described as an oxidative 1,3-dipolar [3+2] cycloaddition,



Scheme 1. Reactions of $[Fe(CO)_3\{R^1N{=}C(H)–(R^3)C{=}X\}]$ ($X{=}NR^1$,O) with electron-deficient alkynes

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[a] University of Amsterdam, Institute of Molecular Chemistry, Department of Inorganic Chemistry,
Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands
Fax: (internat.) + 31-20/525-6456
E-mail: hwf@anorg.chem.uva.nl

[b] Utrecht University, Bijvoet Center of Biomolecular Research, Crystal and Structural Chemistry,
Padualaan 8, 3548 CH Utrecht, The Netherlands

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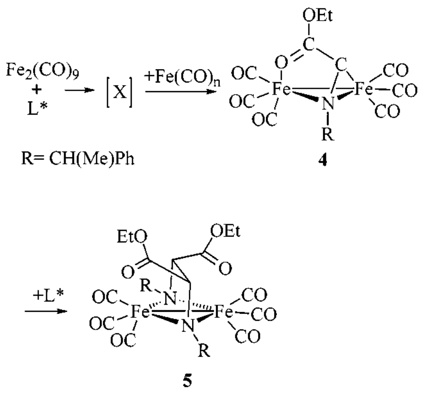
in which the electron-deficient alkyne (dipolarophile) adds across the Fe–N=C fragment (1,3-dipole) to give the bicyclo[2.2.1] intermediate **2**. Subsequent insertion of CO and uptake of an additional ligand (L′), followed by reductive elimination and recoordination of the double bond, results in the formation of the [(1,5-dihydropyrrol-2-one)Fe(CO)$_3$] complexes **3**.

In order to broaden the synthetic potential of this reaction we have investigated the closely related [Fe(CO)$_3$(1-aza-4-oxa-1,3-butadiene)] complexes **6** (cf. Scheme 1; X = O, R^3 = Me, Ph), in order to probe their reactivity towards electron-deficient alkynes.[25,26] To this end we studied the coordination behaviour of α-imino ketones towards carbonyliron compounds.

In contrast to the α-diimine chemistry little is known about the coordination behaviour of α-imino ketones towards d^8-metals. α-Imino ketones have been shown to form monodentate *trans*-[PtCl$_2$(PR$_3$)(R^{1}N=C(R^2)–C(R^3)=O][27] and bidentate [(AlMe$_3$)$_2$(σ,σ-*N,O*–MeN=C(Ph)–C(Ph)=O)] complexes.[28] In these complexes, as well as in the free ligand, the N=C–C=O moiety has a *gauche* conformation with a torsion angle of approximately 90° around the central C–C bond, which is attributed to a minimising of the steric repulsion between the skeleton substituents. The reaction of Fe$_2$(CO)$_9$ with the closely related α-imino ester PhCH(Me)N=C(H)C(OEt)=O (L*), as described by Weiss et al.,[29] resulted in the formation of two dinuclear products, Fe$_2$(CO)$_6$(L*) (**4**) and the C–C coupled complex Fe$_2$(CO)$_6$(L*–L*) (**5**) (cf. Scheme 2).



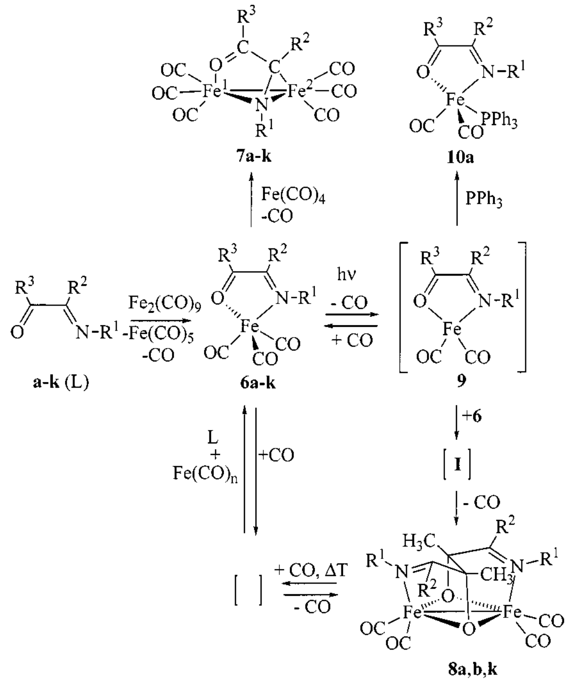
Scheme 2. Reaction of [Fe$_2$(CO)$_9$] with PhCH(Me)N=C(H)–C(OEt)=O (L*)

In complex **5**, a C–C coupling reaction occurs between the imine C atoms of two α-imino ester ligands. This type of C–C coupling has also been observed in the reaction of R-DAB and R-Pyca with carbonylruthenium compounds,[7] leading to [Ru$_2$(CO)$_{4,5}$(R-ADA)] (cf. Table 1) and [Ru$_2$(CO)$_{4,5}$(R-APE)] (cf. Table 1), respectively, but has never been observed for iron.

In this paper we report on the reactions of α-imino ketones (L) with Fe$_2$(CO)$_9$, which results in the formation of the mononuclear chelate complexes [Fe(CO)$_3$(α-imino ketone)] (**6**) and the dinuclear complexes [Fe$_2$(CO)$_6$(α-imino ketone)] (**7**) and [Fe$_2$(CO)$_4$(L–L)] (**8**). Complexes **8** contain two α-imino ketone ligands which are C–C-coupled at the ketone carbon atoms. The influence of the substitution pattern of the α-imino ketone on the formation of the complexes is discussed. The X-ray crystal structures of [Fe(CO)$_3${σ-*N*,σ-*O*-(MeN=C(Ph)–C(Ph)=O)}] (**6g**) and of the newly formed dimeric complex [Fe$_2$(CO)$_4$(*t*BuN=(H)C(Me)C(O)(O)C(Me)C(H)=N*t*Bu)] (**8a**) are described.

Results and Discussion

The α-imino ketones R^{1}N=C(R^2)–C(R^3)=O (L) and the complexes discussed in this investigation are schematically presented in Scheme 3. The type of complex is identified by Arabic numbers. The different α-imino ketones are indicated by the letters **a–k**.



	a	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**	**j**	**k**
R^1	*t*Bu	*t*Am	CH(*i*Pr)$_2$	*p*Tol	*i*Pr	*t*Bu	Me	*p*Tol	*i*Pr	PhCH$_2$	R_1–R_2 =
R^2	H	H	H	H	H	H	Ph	Ph	Ph	Me	-(CH)$_4$-
R^3	Me	Me	Me	Ph	Ph	Ph	Ph	Ph	Ph	Me	Me

Scheme 3. Observed reaction sequence for [Fe$_2$(CO)$_9$] with the α-imino ketones **a–k**

The reaction of [Fe$_2$(CO)$_9$] with the α-imino ketones **a–k** at room temperature results in the formation of the mononuclear chelate complexes [Fe(CO)$_3$(α-imino ketone)] (**6e–h**), the new dinuclear complexes [Fe$_2$(CO)$_6$(α-imino ketone)] (**7a–j**), and the C–C-coupled dimers [Fe$_2$(CO)$_4$(R-ADO)] (**8a**,**b**) (cf. Table 1) and [Fe$_2$(CO)$_4$(R-OPB)] (**8k**) (cf. Table 1). Throughout the text [Fe$_2$(CO)$_4$(L–L)] (**8a,b,k**) is used for these C–C-coupled dimers. The product formation and distribution depends strongly on the substitution pattern of the α-imino ketone and on the solvent.

In all cases the mononuclear chelate complexes [Fe(CO)$_3$(α-imino ketone)] (**6**) are initially formed. However, only when the ligands **e–h** are used are complexes **6** stable enough to be isolated, giving **6h** in moderate yield and **6e–g** in good to high yields. The complexes **6** react with [$Fe(CO)_4$] fragments forming [$Fe_2(CO)_6$(α-imino ketone)] (**7a–j**) in moderate to good yield depending on the α-imino ketone used. In complexes **7** the α-imino ketone is σ-*O*,μ_2-*N*,η^2-C=N-coordinated, donating six electrons to the two iron centres. When R^3 = Me, complexes **6** can also react with another equivalent of the α-imino ketone and the carbonyliron compound leading to the new complexes [$Fe_2(CO)_4$(L–L)] in moderate (**8a,b**) or low (**8k**) yield. In complexes **8**, the two α-imino ketones are reductively coupled through the ketone carbon atoms. The resulting bridging ligand is formally dianionic and donates 10 electrons to the two iron centres. Complexes **8a,b** react readily with carbon monoxide (1 atm) at 80 °C to quantitatively regenerate **6a,b**, which under these conditions are stable. Irradiation of a solution of **6a,b** in the low-energy band results in the reformation of complexes **8a–b** in almost quantitative yield. Irradiation of **6a** in the presence of PPh_3 results in the formation of complex **10a** and complex **8a** is not formed. The formed complexes have been characterised by IR, UV/Vis, ^{1}H- and ^{13}C-NMR spectroscopy, elemental analysis, and X-ray crystal structure determinations for complexes **6g** and **8a**. In the following section we will first discuss the structural data and spectroscopic properties of the relevant complexes and subsequently deal with the aspects of their formation, their stability and their reactivity. A mechanism for the formation of complexes **8** is proposed.

Molecular Structure of σ-*N*,σ-*O*-$Fe(CO)_3$[MeN=C(Ph)C(Ph)=O] (6g)

An ORTEP drawing of the molecular structure of **6g** together with the atomic numbering scheme is shown in Figure 1. Selected bond lengths and angles are given in Table 4 (see Supporting Information). The asymmetric unit of the unit cell contains two crystallographically independent molecules. Since these molecules are nearly identical, only one is discussed here.

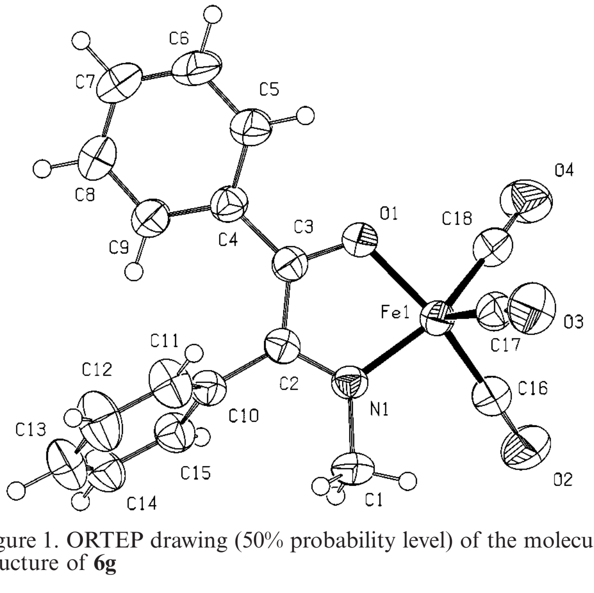


Figure 1. ORTEP drawing (50% probability level) of the molecular structure of **6g**

For a regular five-coordinate d^8 complex, a trigonal-bipyramidal (tbp) or square-pyramidal (sqp) structure might be expected.[40,41] Judging from the angles around the iron atom (cf. Table 4) the coordination around the central iron atom in **6g** more closely resembles a distorted square-pyramidal geometry (89% along the Berry pseudorotation coordinate[42]) with the basal plane defined by N(1), C(16–18), and with Fe(1) 0.353(1) Å above that plane. An ideal tbp or sqp geometry is not possible for these chelate complexes because of the small bite angle of the α-imino ketone (81 ± 1°), a feature also observed in many R-DAB complexes.[40,41,43,44]

The geometries of several five-coordinated [Fe(1,4-dihetero-1,3-butadiene)] complexes, determined by X-ray structures, change from approximately tbp to sqp with increasing π-acceptor properties of the 1,4-dihetero-1,3-butadiene ligand.[44–47] The observed sqp geometry in **6g**, in which the α-imino ketone exhibits good π-acceptor properties, is in agreement with this observation.

The N=C–C=O skeleton is planar within 0.010(3) Å, with the iron atom located 0.03(4) Å above this plane. A similar planar conformation has been found in [$Fe(CO)_2$(*t*-BuNC)(*p*Tol-DAB)],[48] and [$Fe(CO)_3$(MeN=N–N=NMe)].[45] The present example is the first structure showing an intact flat chelate N=C–C=O skeleton, i.e. a conformation with maximum orbital overlap of the C=N and C=O chromophores. From the crystal structure of the free α-imino ketone PhH(Me)CN=C(Ph)–C(Ph)=O, it is known that the N=C–C=O moiety has a torsion angle of 97.7(2)° [46] around the central C–C bond. In monodentate σ-*N*-coordinated *trans*-[$PtCl_2(Et_3)$(*t*BuN=C(H)C(Me)=O]][27] and in the bidentate bridging [$Al(Me_3)_2$-σ,σ′-*N,O*-{MeN=C(Ph)–C(Ph)=O}][28] the torsion angles are 89.0(4)° and 85.9(3)°, respectively (cf. Figure 2). On the basis of these data van Vliet et al.[28] concluded that in the case of α-imino ketones a minimising of the steric repulsion between the ligand substituents is predominant. In [$Fe_2(CO)_6$(PhCH(Me)N=C(H)C(OEt)=O)][29] (**5**) (cf. Scheme 2) an almost flat coordination of the N=C–C=O has been reported; however, in this complex, the N=C imine bond has lost its double-bond character because of the μ_2-*N*,η^2-C=N coordination.

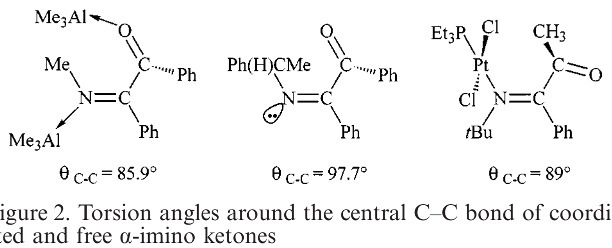


Figure 2. Torsion angles around the central C–C bond of coordinated and free α-imino ketones

The observed planar conformation in **6g** suggests that in the present case the orbital overlap of the imine and ketone moieties, i.e. the formation of a delocalised, low-lying π orbital, prevails over a minimising of the steric interactions between the skeleton substituents. The π*-orbital of the N=C–C=O system, which is antibonding in the C=N and C=O bond and bonding in the central C–C bond, plays an important role for the π-back donation from the electron-rich iron thus allowing the formation of a stable chelate.

Consequently, the coordination of the α-imino ketone to the iron centre in **6g** leads to a significant lengthening of both the imine [C(2)–N(1) = 1.336(3) Å] and the ketone [C(3)–O(1) = 1.295(3) Å] bonds while the central [C(2)–C(3) = 1.410(3) Å] bond is significantly shortened when compared to the C=N, C=O and the central C–C bonds in the free α-imino ketone PhH(Me)CN=C(Ph)C(Ph)=O [1.286(2) Å, 1.209(2) Å and 1.530(2) Å, respectively].[46] The C=O bond is significantly more elongated than the C=N bond (0.086 vs. 0.054 Å), indicating that the chelate coordination exerts a larger effect on the electron density of the C=O than of the C=N bond. This effect is also observed in the ^{13}C-NMR spectra of complexes **8** and might explain the chemoselectivity for C–C coupling at the ketone carbon atom leading to complexes **3** and **8**. Comparable changes in bond lengths, although less pronounced, have been found in [$Fe(CO)_2$(*t*BuNC)(*p*Tol-DAB)][47] and [$Fe(CO)_3$(2,6-*i*$Pr_2C_6H_3$-DAB)].[40] The Fe–C(16), Fe–C(17) and Fe–C(18) distances of 1.771(3) Å, 1.799(3) Å and 1.802(3) Å, respectively, are within the range of normally observed Fe–CO bond lengths.

Molecular Structure of [$Fe_2(CO)_4${*t*BuN=C(H)(Me)C(O)(O)C(Me)(H)C=N*t*Bu}] (8a)

An ORTEP drawing of the molecular structure of [$Fe_2(CO)_4$(*t*Bu-ADO)] (**8a**) (cf. Table 1) together with the atomic numbering scheme is shown in Figure 3. Table 5 (see Supporting Information) gives selected bond lengths and bond angles.The molecule consists of two identical $Fe(CO)_2$ units connected by a metal–metal bond and bridged by the newly formed, formally dianionic 10-electron-donating *t*Bu-ADO ligand. The *t*Bu-ADO ligand has been formed by a reductive C–C coupling of two *t*BuN=C(H)–C(Me)=O ligands through the ketone carbon atoms. As a result of this C–C coupling between C(6)–C(8), the former keto groups C(6)–O(1) and C(8)–O(2) have been reduced to anionic olato groups. The molecule exhibits noncrystallographic pseudo C_2 symmetry with the C_2 axis running through the centres of the C(6)–C(8) and the Fe(1)–Fe(2) bonds.

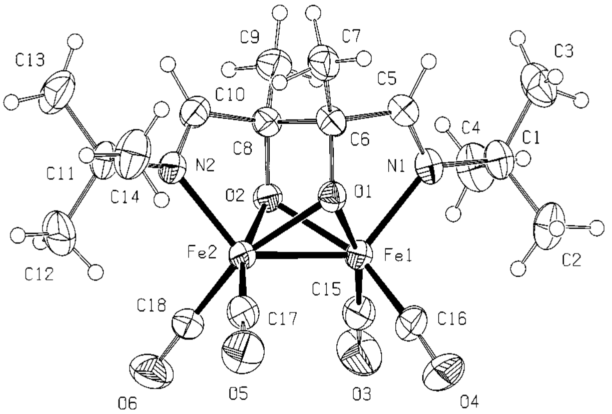


Figure 3. ORTEP drawing (50% probability level) of the molecular structure of **8a**

The Fe(1)–Fe(2) bond length in **8a** is 2.372(2) Å, i.e. a short Fe–Fe bond, since distances in the range of 2.50–2.70 Å are normally observed for single Fe–Fe bonds.[49] The Fe(1)–O(1)–Fe(2) and Fe(1)–O(2)–Fe(2) bond angles are 74.14(14) and 73.78(14)°, respectively, and the Fe–O(carboxylato) bond lengths vary between 1.944(4) and 2.002(4) Å. These bond angles and lengths are comparable to the Fe–X–Fe (X = C, N, O) bond angles and Fe–X (X = C, N, O) bond lengths found in complexes with similar (N,N′), (N,S) and (C,O) bridging ligands.[29,48,50,51] In these complexes comparably short Fe–Fe distances have also been found. The two intact imine moieties are bonded to the iron centre by normal Fe–N=C σ-donor bonds [Fe(1)–N(1) = 2.043(5) Å and Fe(2)–N(2) = 2.030(5) Å]. The angles around the C–C connective bond [C(8)–C(6)–C(5) 107.9(4)° and C(6)–C(8)–C(10) 107.3(4)°] differ only slightly from the optimum value of 109.7° for sp^3-hybridised atoms. In the related complex [$Ru_2(CO)_5$(*i*Pr-ADA)], it was concluded from several structural features that the *i*Pr-ADA ligand is forced to coordinate to the ruthenium centres which might explain the facile thermal rupture of the central C–C bond in this complex.[7] From the observed bond angles and lengths in **8a** it appears that the *t*Bu-ADO ligand exhibits no geometrical constraints that could explain the facile fission of the C(6)–C(8) bond under carbon monoxide. The newly formed C–C connective bond C(6)–C(8) in **8a** of 1.587(8) Å is, however, significantly longer than a normal C(sp^3)–C(sp^3) bond. Comparatively long bond lengths have been reported earlier in complexes containing two C–C-coupled R-DAB or α-imino ester ligands[8,29,52–55] and seem to be characteristic for C–C bonds in N–C–C–N moieties in which both nitrogen atoms are covalently coordinated to the metal centres. On dissolution, the dimer [EtZn(*t*Bu-Pyca)]$_2$ [53,54] dissociates to a very small extent into monomers, thus forming an equilibrium mixture showing the weakness of the C–C connective bond. However, [$Mo_2(CO)_6$(R-ADA)][55] complexes do not split under carbon monoxide.

In conclusion, we can say that the *t*Bu-ADO ligand in **8a** exhibits no geometrical constraint upon coordination to the iron centres, the newly formed central C(6)–C(8) bond [1.587(8) Å] is longer than normal C–C bonds. Whether or not the facile breaking of the central C(6)–C(8) bond, which is an experimental fact, may be explained by the elongation of C(6)–C(8) remains an open question.

IR, UV/Vis Spectroscopy and Elemental Analysis

The IR, UV/Vis and analytical data of the complexes **6**, **7**, **8** and **10a** are listed in Table 6 (see Supporting Information). The IR spectra of complexes **6** show three strong terminal carbonyl absorptions of equal intensity in the ν(CO) region of 2100–1900 cm^{-1}. The CO absorptions of **6e–g**, and even more so of **6h**, are found at higher frequencies than those of **6a,b** indicating that π-back bonding to the terminal carbonyl ligands decreases on going from **6a** to **6h**. This is a result of the better π-accepting capacity of the α-imino ketones going from ligands **a,b** to **e,f** to **g** and **h**, which bear none, one, two or three electron-withdrawing aromatic groups, respectively.

The six terminal carbonyl ligands of $[Fe_2(CO)_6L]$ (**7a–j**) give rise to six medium to strong absorptions in the ν(CO) region. The pattern of the absorptions is identical to that of $[M_2(CO)_6$(R-DAB/R-Pyca)] (M = Fe, Ru, Os and FeRu).[6,56–59] This strongly suggests that these complexes are isostructural, which is corroborated by the ^{1}H- and ^{13}C-NMR- spectroscopic data. The substituents on the α-imino ketone show only a marginal influence on the frequency of the CO absorption bands of complexes **7**.

The IR spectra of complexes **8** show three terminal carbonyl absorptions, two of high and one of medium intensity. The pattern of the CO absorption bands strongly resembles that of the closely related complex $[Ru_2(CO)_4$(R-ADA)],[6,7] which contains a similarly coupled dimer of R-DAB. The absorption bands are shifted to a higher frequency (approximately 10–20 cm^{-1}) than those of $[Ru_2(CO)_4$(R-ADA)]. Similar shifts to higher frequency are observed for $[M(CO)_3$(R-DAB)] and $[M_2(CO)_6$(R-DAB)] on going from iron to ruthenium.

Electronic Absorption Spectra of Complexes 6 and 8

All complexes **6** show an intense band at about 530 nm. A second band is located at about 410 nm and for complexes **6e–h** a third band is present at approximately 348 nm. The pattern of the bands in the UV/Vis spectra of complexes **6** closely resembles those found for the isostructural complex $[Fe(CO)_3$(R-DAB)],[60] except for the shift of approximately 20 nm to lower energy. The polarity of the solvent has almost no influence on the positions of the absorption bands [λ_{max} **6a**; 524 nm (pentane), 526 nm (toluene), 527 nm (THF)]. This lack of solvatochromic behaviour is also found for $[Fe(CO)_3$(R-DAB)][40,60,61] and $[W(CO)_4$(R-DAB)][61] and is attributed to a strong mixing of the metal d-(HOMO) and α-diimine π*-(LUMO) orbitals. As a result these transitions hardly possess any charge-transfer character, and therefore do not show solvatochromic behaviour. On the basis of these similarities, the band at 530 nm is assigned to several electronic transitions within the metallacycle[40,61] rather than to a charge transfer transition from the metal to the α-imino ketone ligand (MLCT). The band at 410 nm is assigned to a LF transition as for $[Fe(CO)_3$(R-DAB)]. The third band at 348 nm observed in **6e–h** is due to an intra-ligand transition.

Complexes **8a,b** possess a weak band at approximately 640 nm (MLCT) and a strong absorption band at 367 nm. The latter is assigned to the σ–σ* transition of the metal–metal bond. This is corroborated by the increase in intensity of this band upon lowering the temperature, an effect which has been observed before for σ–σ* transitions of metal–metal bonds.[62,63]

Elemental Analyses

Except for **6g**, complexes **6** have not been analysed due to their instability and the fact that they cannot be crystallised. No satisfactory elemental analyses could be obtained for complex **7d** because the isolated oil was not analytically pure and no crystals could be obtained. Complex **8k** has not been analysed because the isolated powder was not analytically pure and the complex decomposes on crystallisation.

NMR Spectroscopy

Tables 6 and 7 with the complete ^{1}H- and ^{13}C-NMR-spectroscopic data of complexes **6**, **7** and **8** are available as Supporting Information.

The ^{1}H- and ^{13}C-NMR spectra of **6a–b** were obtained by splitting **8a–b** under carbon monoxide pressure because, due to the instability of **6a–b**, it was not possible to prepare a suitable NMR sample from the reaction mixture (see Experimental Section). The imine proton resonances (**6a**,**b**,**e**,**f**) are observed between δ = 8.74 and δ = 7.61, whereas in the uncoordinated α-imino ketones the imine proton (**a–f**) resonances are observed between δ = 8.1 and δ = 7.2. The imine and ketone carbon atom resonances are shifted by approximately 12–15 and 20–28 ppm to lower frequency, relative to those of the free ligands, as a result of π-back donation into the low-lying delocalised LUMO of the α-imino ketone. Comparable shifts have been observed for $[Fe(CO)_3$(R-DAB)].[64] The large low-frequency shift of the ketone carbon atom in comparison with the imine carbon atom suggests that the chelate coordination exerts a larger effect on the electron density of the ketone carbon atom. This might be the reason for the observed chemoselectivity in the C–C-coupling reactions, i.e. only coupling at the ketone carbon atom is observed resulting in the formation of complexes **8** and **3** (cf. Scheme 1). Furthermore, it is evident from the X-ray crystal structure of **6g** that the C=O bond is significantly more elongated than the C=N bond, which also suggests a larger effect on the C=O bond upon chelate coordination.

In all complexes **6** the three terminal carbonyl ligands give rise to a single resonance between δ = 212.0 and δ = 214.1, indicating that they rapidly interchange on the NMR time scale at 263 K.

The imine proton and carbon atom resonances of complexes **7** are observed between δ = 4.78–3.77 and δ = 65–90, respectively. These large shifts to lower frequency of approximately 4 ppm and 80 ppm are typical for a μ^2-*N*,η^2-C=N coordination of the C=N moiety of the α-imino ketone and have also been observed in $[M_2(CO)_6$(R-DAB)] (M = Fe, Ru, Os and FeRu) complexes.[6,57–59] The resonances of the ketone carbon atoms are only marginally shifted relative to those of the free ligand.

Because of the asymmetric coordination of the α-imino ketone ligand, the six terminal carbonyl ligands in complexes **7** are inequivalent. In a rigid carbonylmetal skeleton this should result in six independent resonances for the carbonyl groups. However, at 263 K complexes **7** show four resonances with relative intensities of 1:3:1:1 going from high to low frequency. This indicates a local scrambling of the carbonyl groups on one metal centre, which has also been observed in $[Fe_2(CO)_6$(R-DAB)] complexes.[65] This exchange process has been demonstrated for complex **7f** in CD_2Cl_2. At 183 K the six carbonyl ligands give rise to six separate signals, showing that at this temperature the terminal carbonyl ligands on both metal centres are at the limit of slow exchange. The individual assignment of the CO resonances to either one of the two $Fe(CO)_3$ moieties is not clear from this dynamic behaviour but can reasonably be deduced from the ^{13}CO-NMR-spectroscopic data of $[FeRu(CO)_6$(R-Pyca)] complexes. From the crystal structure of $[FeRu(CO)_6$(*i*Pr-Pyca)],[59] it is known that the μ_2-*N*,η^2-C=N coordination of the C=N moiety is directed towards the iron centre. In the ^{13}CO-NMR spectra of these complexes recorded at 263 K the Fe–CO signals appeared as one sharp resonance and the Ru–CO signals as three separate resonances. Consequently, in our case, the three signals of equal intensity (263 K) correspond to the μ_2-*N*,σ-*O*-coordinated $Fe^1(CO)_3$ moiety and the broad resonance corresponds to the three carbonyl groups of the $Fe^2(CO)_3$ moiety, which is μ_2-*N*,η^2-C=N-coordinated through the C=N bond of the α-imino ketone (cf. Scheme 3).

In complexes **8a**,**b** the imine-proton and carbon-atom resonances are observed between δ = 7.55–7.80 and δ = 169.5–174.0, respectively, indicating that the imine moiety is σ-*N*-coordinated to the iron centre. The signals of the reductively coupled ketone carbon atoms in **8** accordingly show a pronounced coordination shift (ca. 120 ppm) to lower frequency and are observed around δ = 80. The four terminal carbonyl ligands give rise to two resonances between δ = 217 and δ = 218, indicating pairwise exchange at each iron centre.

Reactions of α-Imino Ketones with Carbonyliron

Complex Formation

The formation, stability and yield of complexes **6**, **7** and **8** strongly depends on the R^1, R^2, and R^3 substituents attached to the imine nitrogen atom, the imine carbon, and the ketone carbon atom, respectively. In the following sections we will first discuss the formation of complexes **6** and **7** and the factors that influence their stability. Subsequently, the formation of complex **8** is discussed and a mechanism is proposed.

Formation and Reactivity of $[Fe(CO)_3$(α-imino ketone)] (6)

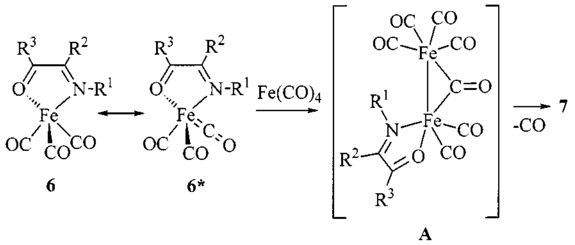
The reaction of $[Fe_2(CO)_9]$ with the α-imino ketones **a–k** at room temperature in THF or toluene results in the initial formation of the deep purple chelate $[Fe(CO)_3$(α-imino ketone)] complexes **6**, probably via a monodenate *N*-coordinated $[Fe(CO)_4$(α-imino ketone)] intermediate, as a result of the better σ-coordinating properties of the C=N moiety than the C=O moiety,[27,66] according to Equation 1.

$$[Fe_2(CO)_9] + \text{α-imino ketone} \rightarrow [Fe(CO)_3(\text{α-imino ketone})]\ (\mathbf{6}) + [Fe(CO)_5] + CO \qquad (1)$$

In THF no formation of **6i** was observed. In toluene, however, low concentrations of **6i** were formed which, under the reaction conditions, rapidly reacts further to **7i**. Analogous to $[Fe(CO)_3$(R-DAB)], complexes **6** are intensely coloured, highly air-sensitive and could not be isolated pure in the solid state except for **6g**. Complexes **6** are soluble and stable in common solvents as hexane, Et_2O, toluene and THF, but decompose in chlorinated solvents like $CHCl_3$, as is the case for $[M(CO)_3$(R-DAB)] (M = Fe, Ru).[7] Complexes **6a**,**b** react photochemically to form the corresponding complexes **8a**,**b**. Irradiation of **6e–g**, however, does not lead to the corresponding C–C coupled complexes **8** but results in slow decomposition of **6e–g**.

Formation and Reactivity of $[Fe_2(CO)_6$(α-Imino Ketone)] (7)

The $[Fe_2(CO)_6$(α-imino ketone)] complexes **7** are formed in THF and toluene by reaction of $[Fe(CO)_3$(α-imino ketone)] (**6**) with $Fe(CO)_4$ (cf. Scheme 4). Complexes **7** are probably formed via the CO-bridged intermediate **A**, similar to the proposed intermediate for the formation of $[Fe_2(CO)_6$(R-DAB)].[67] The formation of **A** can be described as an isolobal analogue[68.69] of the addition of an olefin to a carbene giving a cyclopropane ring system. In the present case, $Fe(CO)_4$ is isolobal with a carbene and the Fe–C bond of a terminal CO ligand in **6** is, in its resonance structure (**6***), isolobal with an olefin. Addition results in the formation of intermediate **A**, and subsequent coordination of the C=N π-bond with concomitant loss of CO completes the structure of complex **7**.



Scheme 4. Proposed reaction mechanism for the formation of **7**

Complexes **7** are isolated as red-brown crystalline solids, except for **7d**, and are air-stable in crystalline form. The stoichiometry of complexes **7** has been established by elemental analyses. The α-imino ketone in complexes **7** is σ-*O*,μ_2-*N*,η^2-C=N-coordinated to the two iron centres and donates six electrons, as can be concluded from the IR, ^{1}H-NMR, and ^{13}C-NMR spectra. An analogous coordination has been found for the closely related α-imino ester complex $[Fe_2(CO)_6\{PhCH(Me)N=C(H)C(OEt)=O\}]$[29] (**5**) (cf. Scheme 2). No formation of the alternative possible six-electron coordination mode, i.e. σ-*N*,μ_2-*O*,η^2-C=O, has been observed. In the α-imino ketone 2-acetylpyridine (**k**), the C=N π-bond is not available for η^2 coordination because it is part of an aromatic pyridine system. Therefore, σ-*N*,μ_2-*O*,η^2-C=O is the only accessible six-electron coordination mode. However, with ketone **k** only complex **8k** is formed and the formation of a complex with a σ-*N*,μ_2-*O*,η^2-C=O coordination mode is not observed. With the closely related α-imino ketones 2-benzoylpyridine and pyridine-2-carboxaldehyde (i.e. bearing a phenyl group and a proton on the ketone carbon atom, respectively) no isolable complexes are formed. Since initially the mononuclear chelate $[Fe(CO)_3\{C_5H_4N\text{-}2\text{-}C(R^3)=NR^1\}]$ complexes are formed, indicated by the deep blue colour of the reaction mixture, this means that either complexes with a σ-*N*,μ_2-*O*,η^2-C=O coordination of the α-imino ketone are not formed, or they decompose under the reaction conditions.

The yields of complexes **7** depend strongly on the ligand used. Generally the yields are higher for the ligands with a phenyl substituent on the ketone carbon atom than for those bearing a methyl group. In the latter case the lowest yields are found for ligands **a** and **b** (ca. 17%). With these ligands, however, complexes **8a,b** are formed in ca. 25% yield leading to a total yield of binuclear complexes of 40 to 45%. Furthermore, it is apparent that when R^1 (the imine nitrogen substituent) is an aryl group the yield is much lower than for R^1 = alkyl. This observation can be accounted for in terms of the lower basicity of the imine donor site for aryl vs. alkyl; if R^1 is aryl, this will lead to a less-efficient μ_2-*N*,η^2-C=N interaction. As a consequence, under these conditions complexes **7d**,**h** react with Fe(CO)$_n$ fragments to give unknown products, which lowers the yields. This has also been found in [$Fe_2(CO)_6$(Aryl-Pyca)] complexes.[70]

Reaction With Free Ligand

Complexes **7** do not react thermally or photochemically with an excess of free ligand. Consequently, **7** is not an intermediate in the formation of **8**.

Reaction With CO

Treatment of [$Fe_2(CO)_6$(R-DAB)] with carbon monoxide (40–50 bar) at elevated temperatures yielded the monomeric complexes [$Fe(CO)_3$(R-DAB)] and [$Fe(CO)_5$].[43,70] This route should also be convenient for the formation of the monomeric [$Fe(CO)_3$(α-imino ketone)] complexes **6**. However, reaction of [$Fe_2(CO)_6$(α-imino ketone)] (**7**) with CO leads only to decomposition, and the monomeric complexes **6** are not detected. The η^2-C=N coordination is probably stronger than the σ-*O* coordination and, consequently, the coordinated keto oxygen atom is substituted by CO, which triggers the decomposition of **7**.

Factors that Influence the Formation and Stability of Complexes 6 and 7

It has been mentioned before that the N=C–C=O skeleton has a conformational preference for a near orthogonality of the N=C and C=O groups (cf. Figure 2), caused by steric interactions of the ligand substituents, especially on the 1,3-and 2,4-positions.[27,28,46]

The crystal structure of **6g** confirms that the α-imino ketone is σ-*N*,σ-*O* chelating in a flat planar *cis* conformation. This planar coordination of an intact N=C–C=O moiety shown in **6g** has never been observed before. So, the primary factor that influences the formation and stability of complexes **6** is whether the α-imino ketone can sterically easily adopt a planar or near planar *cis* conformation. Furthermore, the stability of complexes **6** depends on the σ-donor and π-accepting properties of the α-imino ketone ligand upon coordination. Because the energy of the n-electrons at the oxygen is much lower than at the nitrogen atom, α-imino ketones are weaker donors than diazabutadienes. The unoccupied orbitals of the iron centre are at still higher energy than the n-electrons at the nitrogen atom.[66,71] Consequently, reinforcement of the dative bond by significant π-back donation is required for the formation of stable chelate complexes **6**.[66] The extent of π-back donation depends on the energy level of the π*-LUMO, which in turn can be tuned with the ligand substituents, especially the substituent on the ketone carbon atom. As a consequence, electron-donating groups (like methyl) disfavour chelate coordination, while electron-withdrawing groups (like phenyl) will lead to more stable complexes. It should be noted that when the level of the π*-LUMO is lowered too far in energy this can lead to a redox reaction in which the metal centre is oxidised, leading to decomposition of the formed complexes.[66]

Thirdly, the stability of complexes **6** depends on the propensity of η^2-C=N coordination to a second metal fragment, giving rise to the formation of complexes **7**. The propensity of the analogous R-DAB towards η^2-C=N coordination has been studied by Staal et al.[17] and decreases on going from RCH_2 to R_2CH to R_3C for the imine nitrogen substituent on R-DAB. The propensity towards η^2-C=N coordination will also depend on the substituent on the imine carbon atom and decreases in the order H > Me >> Ph, as has been found in the reactivity of complexes [{C_5H_4N-2-C(R^3)=NR^1}$Fe(CO)_3$] (R^3= H, Me, Ph) towards $Fe(CO)_4$ fragments.[70]

Considering these factors it is understandable that for the α-imino ketones **e–g**, and less so for **h**, the stable complexes **6e–h** are formed. All three have an electron-withdrawing phenyl substituent on the ketone carbon atom which favours the formation of a stable chelate. The α-imino ketones **g** and **h** have relatively small substituents on the imine nitrogen atom and a bulky phenyl substituent on the imine carbon atom, while the α-imino ketones **e,f** have relatively bulky *i*Pr and *t*Bu groups on the nitrogen but only a proton on the imine carbon atom. This means that these α-imino ketones can easily adopt a planar *cis* conformation and subsequently form the stable complexes **6e–h**. The reaction of **6e** → **7e** is more favourable than the reaction **6f** → **7f** because of the greater propensity for η^2-C=N coordination (R_2CH vs. R_3C) of ligand **e**, which is corroborated by the higher yields of **7e**. For the α-imino ketone **h**, the steric influence of the *p*Tol group is similar to that of a cyclohexyl, but electronic influences also play an important role as can be seen from the instability of **7d**,**h** (see above). Complex **6h** slowly decomposes in solution, which could be due to the inferior σ-donating capacity of the nitrogen or to an internal redox reaction because of the low-lying π*-LUMO.

When relatively bulky substituents are attached to both the imine nitrogen and carbon atoms (**c**,**i**) it is difficult for these ligands to adopt the planar *cis* conformation. This is confirmed by the observation that only very low concentrations of **6c**,**i** are formed during the reaction, i.e. no intensive colouring of the reaction mixture is observed. The reaction of α-imino ketone **i** in THF resulted only in the formation of [$Fe(CO)_4$(THF)] and free ligand. Performing the same reaction in toluene, a less coordinating solvent, resulted in the formation of **7i** in good yield by a fast reaction of **6i** with $Fe(CO)_4$. This demonstrates particularly well the poor chelating properties of α-imino ketones when they cannot easily adopt a planar *cis* geometry.

The ligands **a–c** have a methyl substituent on the ketone carbon, a proton on the imine carbon, and a big aliphatic substituent on the imine nitrogen atom. In principle this set of substituents appears sterically suitable for the formation of complexes **6**. However, complexes **6a–c** cannot be isolated in high yield. With ligand **c**, complex **6c** is formed in very low concentrations, i.e. no intense colouring of the reaction mixture is observed. Apparently, the 2,4-dimethyl-3-pentyl substituent on the imine nitrogen atom in ligand **c** is so bulky that the planar *cis* conformation is strongly disfavoured, i.e **6c** is formed in low concentrations and quickly reacts further to form complex **7c** in 38% yield. The reduced yields of **7a**,**b** (ca. 17%) have to be ascribed to the formation of **8a,b** and the sterically disfavoured η^2-C=N coordination due to the tertiary (CR_3) substituent on the imine nitrogen in **a**,**b** as opposed to the secondary substituent (CHR_2) in **c**. The methyl substituent on the ketone carbon atom also contributes to the overall low yields because it restricts the coordination of the oxygen atom through reduced π-back donation. Under the reaction conditions this probably leads to a slow chelate formation and consequently decomposition of the initially formed $[Fe(CO)_4\{R^1N{=}C(R^2){-}C(R^3){=}O]\}]$ complexes which are known to be very labile.[68,69]

Formation and Reactivity of $Fe_2(CO)_4$(L-L) (8a,b,k)

Complexes **8a**,**b**,**k** are synthesised in moderate (**8a,b**) or low (**8k**) yield by reaction of the ligands **a,b,k** with $[Fe_2(CO)_9]$, according to Equation 2.

$$2\,[Fe_2(CO)_9] + 2\ \alpha\text{-imino ketone} \rightarrow [Fe_2(CO)_4(L{-}L)]\ (\mathbf{8}) + 2\,[Fe(CO)_5] + 4\,CO \quad (2)$$

They are isolated as dark green powders and are air-stable (**8a,b**) in their crystalline form. They are readily soluble in toluene, acetone, CH_2Cl_2 and THF. In solution **8a,b** are slightly light-sensitive whereas **8k** is very light-sensitive, especially in chlorinated solvents. Irradiation of the isostructural $[Mo_2(CO)_6(t\text{Bu-ADA})]$ at the Mo–Mo-σ,σ* transition results in the formation of $[Mo_2(CO)_6(t\text{Bu-DAB})_2]$,[63] i.e. fission of the C–C bond. Irradiation of **8a,b** at the high-energy slope (λ = 350 nm) of the metal–metal bond σ,σ* transition (**8a**; λ_{max} = 362 nm), however, leads to a fast (CH_2Cl_2) or slow (THF) decomposition of the starting complexes, and formation of $[Fe_2(CO)_4(\alpha\text{-imino ketone})_2]$ is not observed.

Heating a solution of **8a,b** (0.21 mmol, 50 mL) in toluene under CO at 80 °C for ca. 40 min causes fission of the central C–C bond between the two α-imino ketone ligands and of the metal–metal bond giving the mononuclear complexes **6a,b** in quantitative yield, according to Equation 3.

$$[Fe_2(CO)_4(L{-}L)] + 2\,CO \rightarrow 2\,[Fe(CO)_3(\alpha\text{-imino ketone})] \quad (3)$$

Irradiation of a toluene or THF solution of **6a,b** at the low-energy band (**6a**; λ_{max} = 526 nm) with the 514.5-nm line of an argon ion laser at room temperature leads to reformation of **8a,b** in high yield (cf. Figure 4).

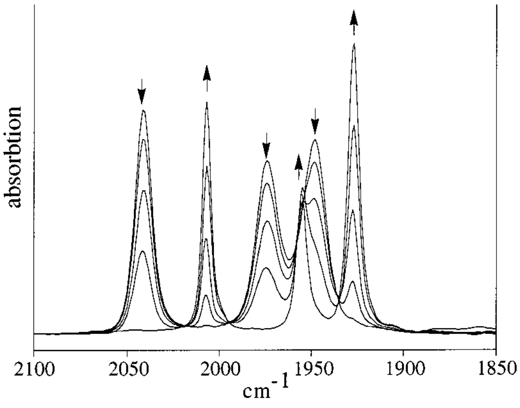
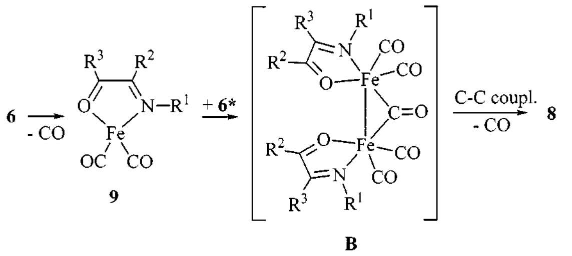


Figure 4. IR-spectral changes in the terminal carbonyl region during the irradiation of $[Fe(CO)_3\{t\text{BuN}{=}C(H){-}C(Me){=}O\}]$ (**6a**) in toluene at 293 K (514.5 nm); formation of **8a**

The irradiation times in THF are longer than those in toluene. The reaction time can be shortened in both cases by purging the solution with nitrogen gas, or degassing the solution under vacuum during irradiation. This observation can be explained by assuming the occurrence of an intermediate (**I** in Scheme 3) with the composition $[Fe_2(CO)_5(\alpha\text{-imino ketone})_2]$, which is formed by the loss of CO from **6a** and subsequent reaction of the highly reactive $[Fe(CO)_2(\alpha\text{-imino ketone})]$ (**9**) with the parent complex **6a**. For intermediate **I**, a metal–metal-bonded structure **B**, containing a bridging CO and two chelating α-imino ketone ligands, can be envisaged. A similar intermediate has been proposed for the formation of $[Ru_2(CO)_{4,5}(\text{R-IAE})]$.[7] The formation of **B**, like the formation of **A**, can be seen as an isolobal analogue to the reaction between a carbene and an olefin (cf. Scheme 5). In the present case, $[Fe(CO)_2(\alpha\text{-imino ketone})]$ (**9**) is a d^8-ML_4 fragment, like $Fe(CO)_4$, and is thus isolobal with a carbene. Subsequent addition to the Fe=C bond in **6*** (isolobal with an olefin, Scheme 4) leads to the formation of **B** which contains, as opposed to intermediate **A**, two chelating α-imino ketones. Reductive C–C coupling of the ketone carbon atoms with concomitant extrusion of CO results in the formation of **8a,b,k**. Further support for structure **B** stems from the formation of the isostructural complexes $[Fe_2(CO)_5(c\text{Hex-DAB})_2]$[60] and $[Ru_2(CO)_5\{CH(i\text{Pr})_2\text{-DAB}\}_2]$[72] upon irradiation of $[Fe(CO)_3(c\text{Hex-DAB})]$ and $[Ru(CO)_3\{CH(i\text{Pr})_2\text{-DAB}\}]$ in hexane at 150 K. However, in these cases no C–C bond formation was observed even upon warming the solution.

In order to obtain spectroscopic proof for the proposed mechanism, low-temperature IR and UV/Vis experiments were carried out. Irradiation of **6a** in 2-MeTHF at –120 °C leads initially to the formation of a single photoproduct and upon longer irradiation in the formation of **8a**. The new photoproduct has two CO stretching frequencies at 1962 and 1881 cm^{-1}, a shift of approximately 75 cm^{-1} to lower frequency with respect to those of **6a**, which points to the



Scheme 5. Proposed reaction mechanism for the formation of **8**

formation of $[Fe(CO)_2(2\text{-MeTHF})\{tBuN{=}C(H){-}C(Me){=}O\}]$ (**9a**·2-MeTHF), i.e. loss of CO. The low-frequency shift is due to the good σ-donor capacity of 2-MeTHF at low temperature. In the UV/Vis spectrum, a new intense band is observed at 496 nm, which means that the ML band is shifted somewhat to higher energy on substitution of CO for 2-MeTHF. Irradiation in the presence of PPh_3 results, under the same conditions (–120 °C) or at room temperature, in the formation of the stable complex $[Fe(CO)_2(PPh_3)\{tBuN{=}C(H){-}C(Me){=}O\}]$ (**10a**) [IR: 1967, 1903 cm^{-1}; UV: 560 nm (cf. Scheme 3)], and complex **8a** is not observed. Thermally (–120 °C), **9a** reacts back to form the parent complex **6a** (95%) and, to a small extent, to **8a** (5%). Irradiation of **6a** in toluene at –80 °C leads, as at room temperature, to the formation of **8a** accompanied by some decomposition; no intermediates are observed. These observations firmly support the proposal that the first step in the photochemical reaction is loss of CO. Depending on the stabilising effect of the σ-donor ligand present in solution, the initially formed labile 16e-$[Fe(CO)_2\{tBuN{=}C(H){-}C(Me){=}O\}]$ intermediate (**9a**) can be trapped and isolated (PPh_3), stabilised at low temperature (2-MeTHF) or allowed to react further to form **8a** (toluene).

Irradiation of **6a** in hexane at –100 °C leads predominantly to **8a** together with a new photoproduct in approximately 10% yield. Due to the limited solubility of **8a** in hexane at –100 °C, and probably also of the new photoproduct, they both precipitate from the solution, thus giving rise to rather weak and broad absorptions. However, it can still be seen that the new photoproduct has a bridging CO ligand (1780 cm^{-1}) and three or four absorptions in the terminal region. This supports the formation of the CO-bridged structure **B**, which is furthermore corroborated by the absorption band at 797 nm in the UV/Vis spectrum. Similarly, $[Fe_2(CO)_5(c\text{Hex-DAB})_2]$ has an absorption band at 740 nm. It must be emphasised, however, that the conclusion that **B** is the only intermediate in the C–C-coupling reaction is not justified, since it was only observed at low concentrations. Extended photochemical studies are needed to obtain more detailed information about the reaction pathway **6** → **8**.

The question as to whether or not structure **B** is also an intermediate in the thermal C–C-coupling (**6** → **8**) or -decoupling (**8** → **6**) reaction is difficult to answer. It was mentioned earlier that complexes **6a,b** are stable in the pure form, i.e. they do not react back to their corresponding complexes **8**. As a consequence, under the reaction conditions, complexes other than **6** must play a role in the reaction pathway **6** → **8**. The decoupling reaction of **8a,b** → **6a,b** has been followed by means of high-pressure ^1H-NMR spectroscopy (see Experimental Section). However, an intermediate has not been observed during the conversion from **6** → **8**. It seems likely, however, that an intermediate like structure **B** should also be present in the thermal reaction.

As shown earlier, the C–C-coupled complexes **8** are only formed with ligands **a,b** and **k** which all bear a methyl substituent on the ketone carbon atom, whereas for the corresponding phenyl-substituted ligands **e** and **f** C–C coupling is not observed. Apparently, the methyl substituent is of decisive importance for the formation of **8**. This effect is most probably due to electronic factors (see below), although steric reasons cannot be excluded. The exclusive coupling at the ketone carbon atom is in line with the 1,3-dipolar reactivity, i.e. exclusive addition at the Fe–O=C fragment is observed (cf. Scheme 1). From this it might be concluded that the factors which determine the reactivity for 1,3-dipolar cycloadditions and the C–C coupling reactions discussed here are possibly similar. It has been shown that the 1,3-dipolar reactivity[26,73–75] decreases upon exchange of an electron-donating substituent for an electron-withdrawing substituent (Me → Ph). So analogously, the reactivity for C–C coupling to form **8** might decrease in this order. With ligand **j** the corresponding C–C-coupling product **8j** is not observed which is probably due to steric interactions of the methyl groups on both the ketone and the imine carbon atoms.

The yields of **8a,b** in the thermal reaction are almost identical in THF and toluene. On first sight, lower yields are expected in THF due to its better σ-donor capacity, thus stabilising $[Fe(CO)_2(\alpha\text{-imino ketone})]$, i.e. less-effective formation of intermediate **B** and accordingly **8**. However, in THF higher concentrations of $[Fe(CO)_3(\alpha\text{-imino ketone})]$ are present which results in a more effective formation of intermediate **B**. This is in agreement with the observation that $[Fe_2(CO)_5(c\text{Hex-DAB})_2]$ is only formed at rather high concentrations of $[Fe(CO)_3(c\text{Hex-DAB})]$. Furthermore, this is in line with the observation that **8c** is not formed as **6c** is present in very low concentration. Interestingly, the reaction of ligand **k** with $[Fe_2(CO)_9]$ in THF does not lead to **8k**, while in toluene it is formed in low yield. Obviously, in this case, THF inhibits the formation of **8k**.

Experimental Section

General Remarks: ^1H- and ^{13}C-NMR spectra were recorded with a Bruker AMX-300 spectrometer. Chemical shifts are reported relative to TMS (δ = 0) in the deuterated solvents indicated. – The IR spectra were recorded with a BioRad FTS-7 FTIR spectrophotometer or with a Perkin–Elmer 283 IR spectrophotometer. – Electronic absorption spectra were measured with a Perkin–Elmer Lambda 5 UV/Vis spectrophotometer or with a Varian Cary 4E spectrophotometer. – For low-temperature IR and UV/Vis measurements an Oxford Instruments DN 1704/54 liquid-nitrogen cryostat was used. The irradiations were carried out using the 514.5-nm line of an SP 2025 argon ion laser or a Philips HPK 125-W high pressure mercury lamp equipped with the appropriate interference (λ = 500 nm) filter. – Elemental analyses were carried out by Dornis und Kolbe, Microanalytisches Laboratorium, Mülheim a. d. Ruhr, Germany. All solvents were carefully dried and distilled under nitrogen before use. All preparations were carried out under dry nitrogen by conventional Schlenk techniques. – Silica gel for column chromatography (Kieselgel 60, 70–230 mesh, E. Merck, Darmstadt, Germany) was dried and activated prior to use by heating to 180 °C under vacuum for 16 h. $Fe_2(CO)_9$[30] and the α-imino ketones **a**,**b**,**d–i**[31,33] were prepared according to published procedures. $Fe(CO)_5$ (Strem Chemicals) and 2-acetylpyridine (**k**) (Janssen) were used as commercially obtained.

The new α-imino ketone **c**, having R^1 = 2,4-dimethyl-3-pentyl [CH(*i*Pr)$_2$] (cf. Table 1), R^2 = H, R^3 = Me, was synthesised according to the literature procedure for ligands **a**,**b**.[33] Yield 65%. – IR (pentane, cm^{-1}): $\tilde{\nu}$ = 1708 (vs) ν(C=O), 1650 (m) ν(C=N). – ^1H NMR ($CDCl_3$, room temp.): δ = 7.46 (s, 1 H, N=C*H*), 2.51 (t, *J* = 6.0 Hz, 1 H, N–C*H*), 2.39 (s, 3 H, C*H*$_3$), 2.06 (dsept, *J* = 6.0 Hz, 6.9 Hz, 1 H, C*H*), 0.83, 0.82 [d, *J* = 6.9 Hz, 2 × 6 H, CH(C*H*$_3$)$_2$]. – ^{13}C NMR ($CDCl_3$, room temp.): δ = 199.1 (*C*=O), 159.5 (*C*=N), 83.2 (N–CH), 29.6 (C–CH), 25.03 (*C*H$_3$), 20.5, 18.4 [CH(*C*H$_3$)$_2$].

The explanations for the acronyms used in this paper are given in Table 1.

The general procedures for the preparation of complexes **6e–h**, **7a–j** and **8a,b,k** are given below, details are listed in Table 2.

Table 2. Syntheses of complexes **6e–h**, **7a–j** and **8a**,**b**,**k**

	Ligand substituents			Ligand (mmol)[a]	$Fe_2(CO)_9$ [g, (mmol)]	Solvent (reaction time)[b]	Elution ratio[c]	Yield (%)[d]
Compd.	R^1	R^2	R^3					
6e	*i*Pr	H	Ph	2.65	1.3 (3.60)	THF (1)		75
6f	*t*Bu	H	Ph	2.64	1.2 (3.30)	THF (1)		90
6g	Me	Ph	Ph	2.24	2.5 (6.96)	THF (2)		70
6h	*p*Tol	Ph	Ph	1.67	1.3 (3.60)	THF (0.5)		30
7a	*t*Bu	H	Me	3.73	3.1 (6.52)	THF (3)	7:1	16
7b	*t*Am	H	Me	3.74	3.0 (6.24)	THF (3)	7:1	16
7c	CH*i*Pr$_2$	H	Me	2.75	2.6 (7.14)	THF (3)	7:1	36
7d[e]	*p*Tol	H	Ph	2.24	2.0 (5.50)	THF (2)	7:1	17
7e	*i*Pr	H	Ph	2.65	2.1 (5.70)	THF (3)	7:1	63
7f	*t*Bu	H	Ph	2.64	3.0 (6.24)	THF (3)	7:1	57
7g[f]	Me	Ph	Ph	2.24	2.5 (6.67)	Tol (14)	6:2	75
7h[e]	*p*Tol	Ph	Ph	1.67	1.6 (4.37)	Tol (14)	7:1	25
7i[e]	*i*Pr	Ph	Ph	1.77	2.2 (6.00)	Tol (14)	6:2	64
7j	Benzyl	Me	Me	2.65	2.6 (7.70)	THF (3)	6:4	44
8a	*t*Bu	H	Me	3.73	3.1 (6.52)	THF (3)	2:3	25
8b	*t*Am	H	Me	3.54	3.0 (6.24)	THF (3)	2:3	27
8k[g]	2-Pyridine		Me	4.13	3.0 (6.24)	Tol (14)	3:2	4

[a] Based on 0.5 g of the respective α-imino ketone. – [b] Solvent used, THF (tetrahydrofuran) or Tol (toluene) and the reaction time in hours. – [c] Ratio of pentane/Et_2O for elution of **7a–i** and the ratio of Et_2O/CH_2Cl_2 for elution of **8a**,**b**,**k**. – [d] Yield based on α-imino ketone consumed. – [e] After the reaction was stopped air was bubbled through the solution for 5 min to destroy the mononuclear [$Fe(CO)_3$(α-imino ketone)] complex present. – [f] Green-brown fraction, crystallisation from pentane/Et_2O (5:1) yields a green brown micro crystalline precipitate. – [g] Reaction mixture turned intensively blue.

Synthesis of [$Fe(CO)_3$(α-imino ketone)] (6e–h): To a stirred suspension of [$Fe_2(CO)_9$] in 40 mL of THF was added 0.5 g of the respective α-imino ketone (cf. Table 2), whereupon the solution immediately turned dark purple. After all the free ligand had been consumed [monitored by the decrease of the ν(C=O) band of the ligand], the solution was filtered to remove the unchanged [$Fe_2(CO)_9$]. The solution was concentrated to dryness and the residue was redissolved in 60 mL of pentane (**6e–g**) or 30 mL of pentane/5 mL Et_2O (**6h**) and filtered again. For **6e,f** the solution was concentrated to dryness, yielding **6e,f** as deep purple oils in 80% (**6e**) or 90% (**6f**) yield. Due to their instability these complexes are best used directly after preparation or stored in pentane solution at –30 °C. Cooling a pentane solution of **6g** to –20 °C resulted in dark purple lustrous crystals in about 35% yield, which were suitable for X-ray diffraction. Subsequent crystallisation from a concentrated mother liquor at –30 °C led to a second batch of crystals of **6g** (35%), giving a total yield of 70%. The second batch of crystals often contained small amounts of [$Fe_2(CO)_6$(L)] (**7g**, < 5%), also formed under these reaction conditions. Cooling the pentane/Et_2O solution of **6h** to –30 °C resulted in a red voluminous precipitate, and **6h** was isolated as a pink-red powder in about 30% yield containing small amounts of [$Fe_2(CO)_6$(L)] (**9h,** <5%). Complex **6h** decomposes within 1 d at room temperature and should be stored at temperatures below –20 °C. Due to the instability of **6e,f,h**, and the fact that they cannot be crystallised, no elemental analyses could be obtained.

Synthesis of [$Fe(CO)_3${*t*AmN=C(H)–C(Me)=O}] (6b): Solutions of **6b** to be used in situ for further reactions were synthesised according to the literature procedure for **6a** (cf. Table 1).[25,26]

Synthesis of [$Fe_2(CO)_6$(L)] (7a–j) and [$Fe_2(CO)_4$(L–L)] (8a,b,k): To a stirred suspension of [$Fe_2(CO)_9$] in 40 mL of THF or toluene was added 0.5 g of the respective α-imino ketone (cf. Table 2), whereupon the solution turned dark purple (**a**,**b**) or blue (**k**). The reaction mixture was stirred for 3 h (THF) or 16 h (toluene) during which time the colour of the reaction mixture changed from dark purple/blue to red-brown. After evaporation of the solvent, the residue was redissolved in a minimum of CH_2Cl_2 and the products were purified by column chromatography on silica gel (column 1 × 15 cm). Elution with pentane afforded a green fraction, containing [$Fe_3(CO)_{12}$]. Further elution with pentane/Et_2O (ratio cf. Table 2) afforded a red-brown fraction which, after evaporation of the solvent, gave [$Fe_2(CO)_6$(L)] (**7a–j**) as a red-brown oil or powder. Crystallisation from pentane at –60 °C resulted in most cases in red-brown crystalline products, the yields varied between 15 and 75% (isolated product) depending on the ligand. Subsequent elution with Et_2O/CH_2Cl_2 (ratio cf. Table 2) afforded a dark green fraction which, after evaporation of the solvent, yielded [$Fe_2(CO)_4$(L–L)]

Table 3. Crystallographic data for **6g** and **8a**

Compound	**6g**	**8a**
Empirical formula	$C_{18}H_{13}FeNO_4$	$C_{18}H_{26}Fe_2N_2O_6$
Molecular mass	363.15	478.11
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
Crystal system	triclinic	triclinic
a [Å]	10.6110(14),	7.974(2)
b [Å]	12.1544(13),	11.377(14)
c [Å]	14.5221(11)	13.525(10)
α [°]	88.96(1)	74.24(9)
β [°]	75.20(1)	78.95(4)
γ [°]	67.75(1)	69.98(7)
V [Å^3]	1669.6(4)	1104(2)
Z	4	2
$D_{\text{calcd.}}$ [g cm^{-3}]	1.445(3)	1.439(2)
F(000)	744.0	496.0
μ [cm^{-1}]	9.2	13.5
Crystal size [mm]	0.52 × 0.63 × 0.20	0.10 × 0.20 × 0.75
Data collection		
Temperature [K]	295	295
θmin/θmax [°]	1.5, 27.50	1.57, 27.50
Radiation (monochromated)	Mo-K_α (graphite), 0.71073 Å	Mo-K_α (graphite), 0.71073 Å
Δω [°]	0.83 + 0.35tanθ	0.53 + 0.35tanθ
Horizontal and vertical aperture [mm]	2.95, 4.0	3.0, 4.0
X-ray exposure time [h]	51	35
Linear decay (%)	1.0	1.0
Reference reflections	–2 3 0, 4 2 5, 5 3 2	2 2 3, 3 2 –2, –2 4 2
Index ranges	h: –13 – 13	h: 0 – 10
	k: –15 – 15	k: –13 – 14
	l: –18 – 18	l: –17 – 17
Total data	8495	5445
Unique data	7610	5077
Observed data	6062 [$I > 2.5\sigma(I)$]	3706 [$I > 2.5\sigma(I)$]
Refinement		
No. of refl. and params.	6062, 441	3706, 278
Weighting scheme	$w = 1.0/[\sigma^2(F)]$	$w = 1.0/[\sigma^2(F) + 0.000699\ F^2]$
Final R, wR, S	0.0380, 0.0418, 0.80	0.0546, 0.0791, 1.10
Isotr. therm. par. H atoms [Å^2]	0.075(2)/0.095(5) for CH/CH_3	0.081(4)
$(\Delta/\sigma)_{\text{av}}$ in final cycle	0.0222	0.0142
min./max. resd. density [e/Å^3]	–0.45, 0.45	–0.83, 0.95

(**8a,b,k**) as a green powder. Crystallisation from pentane/CH_2Cl_2 (2:3) resulted in dark green needles of **8a,b**, in 25 and 27% yield, respectively. Crystals of **8a** were suitable for X-ray diffraction. Complex **8k** was formed in only 4% yield and decomposed on crystallisation.

Preparation of Solutions of 6b for ^{1}H- and ^{13}C-NMR Spectroscopy: A solution of ca. 80 mg **8b** in 2.5 mL of [D_6]acetone was placed in a high-pressure NMR tube and kept at 313 K for 5 h under 35 bar carbon monoxide. This resulted in a complete conversion into **6b**.

Reaction of [$Fe_2(CO)_4$(L–L)] (8a,b) with Carbon Monoxide. – Formation of 6a,b: Compound **8a** (0.100 g, 0.21 mmol) or **8b** (0.106 g, 0.21 mmol) was dissolved in 50 mL of toluene and stirred under carbon monoxide for 40 min at 80 °C. During this time the colour of the solution turned from green to intense purple. The reaction was followed by IR spectroscopy and showed that **8a,b** had been quantitatively converted into **6a–b**.

Photochemical conversion of [$Fe(CO)_3$(L)] (6a,b) in [$Fe_2(CO)_4$(L–L)] (8a,b): A toluene solution containing **6a,b** (0.21 mmol, 50 mL) was irradiated into the high-energy slope of the low-energy band (λ_{max} = 526 nm) with the 514.5-nm line of an argon ion laser at room temperature. The reaction was followed by IR spectroscopy. Complete conversion of **6** to **8** took approximately 1 h, during which time the colour of the solution gradually changed from intense purple to green/brown. Due to some decomposition of **6a,b**, the formed products **8a,b** had to be purified by column chromatography. Elution with CH_2Cl_2 afforded a dark green fraction which, after evaporation of the solvent, yielded [$Fe_2(CO)_4$(L–L)] (**8a,b**) as a green powder in 90% yield.

X-ray Crystal Structure Determination of 6g and 8a: Dark opaque crystals were mounted under nitrogen in a Lindemann glass capillary (**6g**) or glued on a glass fibre (**8a**) and transferred to an Enraf–Nonius CAD-4T rotating-anode diffractometer for data collection. Unit-cell parameters were determined from least-squares treatment of the SET4 setting angles of 25 reflections and were checked for the presence of higher lattice symmetry.[34] The crystals of **6g** and **8a** show broad reflection profiles. All data were collected with ω/2θ scan mode, and were corrected for Lp and for the observed linear decay of the intensity control reflections; redundant data were merged into a unique data set. An empirical absorption correction was applied for both compounds with the DIFABS[34] method (correction range 0.646–1.440 for **6g** and 0.614–1.180 for **8a**). The structures were solved with either standard Patterson methods (**8a**) or direct methods (**6g**) (SHELXS86)[35] and subsequent difference Fourier syntheses. Refinement on F was carried out by full-matrix least-squares techniques. A small cavity at 0,0,1/2 of 49 Å^3 was found in the unit cell of **8a**. However, no significant residual density could be detected in that area (PLATON).[36] Hydrogen atoms were introduced at calculated positions [C–H = 0.98 Å] and included in the refinement riding on their carrier atoms. All non-H atoms were refined with anisotropic thermal parameters, H atoms were refined with common isotropic thermal parameters. Weights were introduced in the final refinement cycles. Neutral atom scattering factors were taken from[37] and corrected for anomalous dispersion.[38] All calculations were performed with SHELX76[39] and the PLATON package[36] (geometrical calculations and illustrations) on a DEC-5000 cluster. Crystal data and numerical details of the structure determinations are given in Table 3.

Supporting information for this article (Tables 4 and 5 with selected bond lengths and angles for **6g** and **8a**, Table 6 with IR, UV/Vis, and analytical data, and Tables 7 and 8 with ^{1}H- and ^{13}C-NMR-spectroscopic data for compounds **6**, **7**, and **8**) is available on the WWW under http://www.wiley-vch.de/home/eurjic or from the author. Crystallographic data (excluding structure factors) for the structures of **6g** and **8a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-137484 (**8a**), and -137485 (**6g**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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