

**1,3-Dipolar Cycloaddition Reactions to the C=X—M
Fragment. 9. Synthesis and Characterization of
Mononuclear Imino Ketone Complexes
Fe(CO)₃(*t*-Bu—N=C(H)—C(R)=O) and Their Use in
Chemoselective Cycloaddition Reactions with Dimethyl
Acetylenedicarboxylate Resulting in the Formation of
Fe(CO)₃(butenolide) Complexes**

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Reaction of Fe₂(CO)₉ at room temperature in THF with the α -imino ketones *t*-Bu—N=C(H)—C(R)=O (R = Ph, Me) results in initial formation of mononuclear Fe(CO)₃(*t*-Bu—N=C(H)—C(R)=O) (**9**) in moderate (**9b**: R = Me) to high (**9a**: R = Ph) yield. The σ -O, σ -N chelate coordination behavior of the heterodiene ligand in complexes **9** was confirmed by the spectroscopic data (IR, ¹H and ¹³C NMR). With respect to their spectroscopic properties and chemical behavior the Fe(CO)₃(α -imino ketone) complexes closely resemble the related Fe(CO)₃(R—DAB) complexes. Under the conditions of their formation, complexes **9** undergo subsequent reactions with Fe(CO)_n fragments or free ligand, giving rise to the formation of the stable dinuclear complexes Fe₂(CO)₆(*t*-Bu—N=C(H)—C(R)=O) (R = Ph, Me) and Fe₂(CO)₄(L—L) (**10**) (R = Me). Reaction of the mononuclear Fe(CO)₃(*t*-Bu—N=C(H)—C(R)=O) complexes (**9**) with dimethyl acetylenedicarboxylate at -78 °C under an atmosphere of CO results in the formation of the Fe(CO)₃(butenolide) complexes (**13a,b**), which have been characterized both spectroscopically (IR, ¹H and ¹³C NMR) and by elemental analysis. The solid state structure of complex **13b** was determined by single-crystal X-ray diffraction. Crystals of **13b**, C₁₇H₁₉NO₉Fe, are triclinic, space group *P*1, with cell constants *a* = 8.627(1) Å, *b* = 9.597(2) Å, *c* = 11.557(1) Å, α = 81.60(1)°, β = 88.75(1)°, γ = 83.19(2)°, *V* = 939.8(2) Å³, *Z* = 2, *R* = 0.0405 (*R*_w = 0.0669) for 4165 unique reflections with *I* > 2.5 σ (*I*). The coordination geometry around the central iron atom in **13b** is distorted trigonal bipyramidal, with the intact σ -donating imine nitrogen and the η^2 -coordinated endocyclic C=C bond of the newly formed butenolide ligand occupying axial and equatorial positions, respectively. The proposed initial step in the formation of **13** is a chemoselective 1,3-dipolar cycloaddition of DMADC to the Fe—O=C fragment, yielding a bicyclo[2.2.1] intermediate **11**. As opposed to the similar reactions of related M(CO)₃(R—DAB) complexes, no intermediates can be observed in the present case, because the subsequent CO insertion into the Fe—O bond and the product forming reductive elimination of the newly formed Fe—C bonds are too fast even at very low temperatures.

Introduction

Reactions of complexes M(CO)₂L(R—DAB)¹ (M = Fe, Ru; L = CO, CNR) with activated alkynes (DMADC, MP)¹ have been shown to give synthetically interesting coordinated heterocycles, e.g. 1,5-dihydropyrrol-2-one (**4**) and 1,4,3a,6a-tetrahydropyrrolo[3,2-*b*]pyrrole (**5**) complexes (cf. Scheme I). In the previous parts²⁻⁹ of this series we

have reported on the influence of the coligands, additional ligands (L'), the metal, and the substitutional pattern of the R—DAB ligand on the product formation for this type of reaction.

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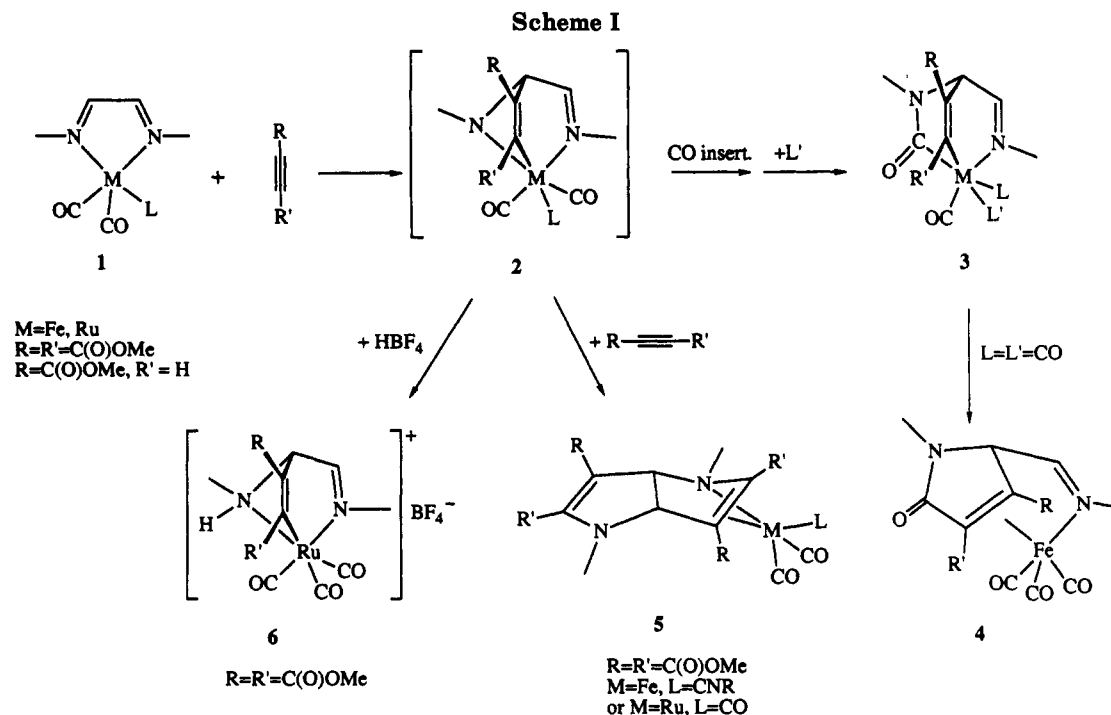
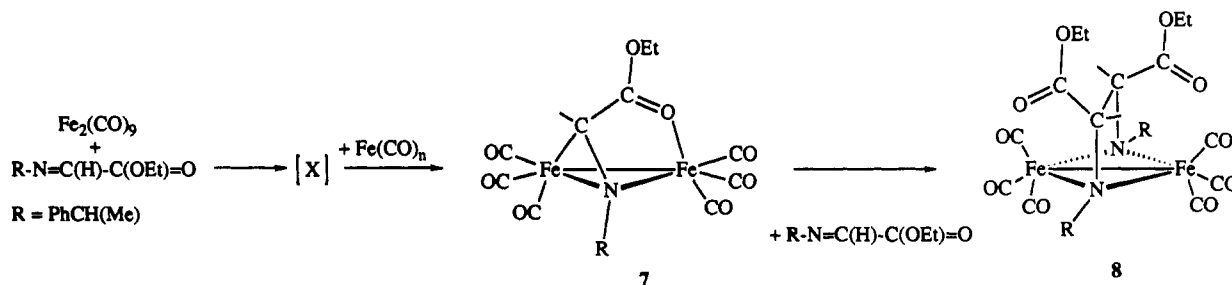
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(1) The abbreviations used throughout this text are as follows. The 1,4-diaza-1,3-butadienes of formula RN=C(H)C(H)=NR are abbreviated as R-DAB. R-ADA stands for 1,6-di-R-1,6-diazahexa-1,5-diene-3,4-di-R-aminato, RN=C(H)(H)C(NR)(H)C(NR)C(H)=NR, the reductively C—C coupled formally dianionic dimer of R-DAB ligated to two metal atoms. 1,4,3a,6a-Tetrahydropyrrolo[3,2-*b*]pyrrole is abbreviated as THPP. Dimethyl acetylenedicarboxylate is abbreviated as DMADC. Methyl propynoate is abbreviated as MP.

**Scheme II**

The initial step in these reactions is described as an oxidative 1,3-dipolar [3 + 2] cycloaddition¹⁰ of the activated alkyne (acting as the dipolarophile) with the $M-N=C$ fragment (the 1,3-dipole), which results in formation of the bicyclo[2.2.1] intermediate **2**. This mechanism is supported both by the isolation of ruthenabicyclo[2.2.1] complex **6** and $M(CO)_2L$ (THPP) (**5**) as well as by a LT-FTIR study.^{7,8} The subsequent reaction of this bicyclo[2.2.1] intermediate and formation of the different products are mainly governed by the variations mentioned above, as can be seen from Scheme I.

In order to study if the concept of organometallic 1,3-dipolar cycloadditions could be applied more generally to other chelate-coordinated heterodiene complexes, we attempted the syntheses of mononuclear σ -N, σ -O chelate $Fe(CO)_3(t-Bu-N=C(H)-C(R)=O)$ complexes to probe their reactivity toward activated alkynes. These $Fe(CO)_3$ -(α -imino ketone) complexes, provided that they react with activated alkynes, would furthermore allow the investigation of the chemoselectivity, i.e., whether the dipolarophile preferentially reacts with either the $Fe-O=C$ or the $Fe-N=C$ fragment.

In contrast to the α -diimine ligands relatively little is known about the coordination behavior of α -imino ketones toward d^8 -metals. The α -imino ketones have been shown to react with *trans*-[PtCl₂(PR₃)₂]₂ under formation of monodentate σ -N-coordinated *trans*-[PtCl₂(PR₃)(RN=C(H)-C(R)=O)] complexes.¹¹ Chelate coordination behavior of the α -imino ketones has been proposed for the

initial intermediate in the reaction with the ZnR_2 complexes.¹² The chelate coordination immediately triggers a single inner-sphere electron transfer from a filled $Zn-R$ bond into the LUMO of the heterodiene ligand, generating a radical pair ($R^{\bullet}-^{\bullet}(imino\ ketone)ZnR$). Recombination of this radical pair results in alkylation of either the ketone carbon or the nitrogen atom depending on the nature of the R group. Reaction of the closely related α -imino ester $PhCH(Me)N=C-C(OEt)=O$ with $Fe_2(CO)_9$, as described by Weiss et al., resulted in the formation of the dinuclear products $Fe_2(CO)_6L$ (**7**) and $Fe_2(CO)_6(L-L)$ (**8**) (cf. Scheme II).^{13,14}

In this paper we report on the reactions of $t-Bu-N=C(H)-C(R)=O$ ($R = Me, Ph$) with $Fe_2(CO)_9$, resulting in initial formation of chelate $Fe(CO)_3$ (1-oxo-4-aza-1,3-butadiene) complexes (**9**). Subsequent reaction of $Fe(CO)_3$ -

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(10) In part 5 of this series the isolobal analogy between the $C=N-Fe$ fragment and an azomethine ylide, as a typical representative of a Huisgen 1,3-dipole, is demonstrated. The literal 1,3-dipole results from localizing two of the four electrons at the onium center Y, which gives rise to the sextet structures $^+X-Y-Z^- \leftrightarrow ^-X-Y-Z^+$.

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(*t*-Bu—N=C(H)—C(R)=O) with free ligand and an Fe(CO)_n fragment under the reaction conditions results in the formation of stable dinuclear species. Furthermore we report on the reactions of the Fe(CO)₃(*t*-Bu—N=C(H)—C(R)=O) complexes (9) with dimethyl acetylenedicarboxylate, resulting in formation of the Fe(CO)₃(butenolide) complexes (13a,b). The X-ray crystal structure of complex 13b is described and compared to that of the isoelectronic Fe(CO)₃(1,5-dihydropyrrol-2-one) (4). The initial step in the formation of complexes 13 will be discussed in terms of a chemoselective 1,3-dipolar cycloaddition of the activated alkyne to the Fe—O=C fragment. An explanation for the observed reaction rate is proposed, which is based on the isolobal relationship of the Fe—X=C (X = N, O) fragment with the classical organic 1,3-dipoles azomethine and carbonyl ylide.

Experimental Section

Materials and Apparatus. ¹H and ¹³C NMR spectra were obtained on Bruker AC-100 and AMX-300 spectrometers. The IR spectra were recorded with a Perkin-Elmer 283 IR spectrophotometer. Electronic absorption spectra were measured on a Perkin-Elmer Lambda 5 UV/vis spectrophotometer. Elemental analyses were carried out by the section Elemental Analysis of the Institute for Applied Chemistry, TNO, Zeist, The Netherlands. The solvents were carefully dried and distilled under nitrogen prior to use. All preparations were carried out under an atmosphere of 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. The α-imino ketones (*t*-Bu—N=C(H)—C(R)=O) (R = Ph, Me) have been prepared according to published procedures.¹⁵ Dimethyl acetylenedicarboxylate (DMADC) was used as purchased from Aldrich.

Synthesis of Fe(CO)₃(*t*-Bu—N=C(H)—C(Ph)=O) (9a). A 1-mL (5.8-mmol) aliquot of *t*-Bu—N=C(H)—C(Ph)=O was added to a suspension of 2.7 g (7.4 mmol) of Fe₂(CO)₉ in 80 mL of THF. Immediately after addition the color of the solution changed from light orange to deep purple. After stirring for approximately 1 h at room temperature, all the *t*-Bu—N=C(H)—C(Ph)=O had reacted (monitored by the decrease of the ν(C=O) IR band at 1665 cm⁻¹) and the solution was filtered to remove excess Fe₂(CO)₉. The solution was evaporated to dryness, and the residue was redissolved in 80 mL of pentane. After cooling to -80 °C, the solution was filtered again to remove the small amount of dimeric Fe₂(CO)₆(*t*-Bu—N=C(H)—C(Ph)=O) also formed under the reaction conditions. The solution was evaporated to dryness, yielding 1.7 g (5.2 mmol, 90%) of complex 9a. Due to the instability of this complex no elemental analysis was obtained.

Synthesis of Fe(CO)₃(*t*-Bu—N=C(H)—C(Me)=O) (9b). A 3.3-mL (23-mmol) aliquot of *t*-Bu—N=C(H)—C(Me)=O was added to a suspension of 11.2 g (31 mmol) of Fe₂(CO)₉ in 225 mL of THF. After stirring for 30 min at room temperature, the solution was filtered to remove the unreacted Fe₂(CO)₉ (5.75 g). After the solvent was evaporated, the oily residue was kept under reduced pressure for a short period to remove Fe(CO)₅ and was then redissolved in 80 mL of pentane. The solution was cooled to -80 °C and filtered to remove the dinuclear complexes Fe₂(CO)₆L and Fe₂(CO)₄(L—L) also formed during the reaction. The deep purple solution, which contains ca. 8 mmol (50–55%) of Fe(CO)₃(*t*-Bu—N=C(H)—C(Me)=O) (9b), was used as such because removal of the solvent again results in formation of small amounts of dinuclear products. Due to the instability of this complex no elemental analysis was obtained.

Synthesis of Fe(CO)₃N(*t*-Bu)=C(H)—C(Ph)C(CO₂-

CH₃)=C(CO₂CH₃)C(O)O (13a). A freshly prepared solution of 5.2 mmol of Fe(CO)₃(*t*-Bu—N=C(H)—C(Ph)=O) (9a) in 80 mL of pentane (*vide supra*) was cooled to -78 °C under an atmosphere of CO and a solution of 650 μL (5.3 mmol) of DMADC in 40 mL of pentane/diethyl ether (4:1) was added dropwise during ca. 45 min. After the solution was stirred for an additional 2 h at -78 °C, the intensely purple solution had turned pale purple and the purple-brown crude product precipitated. The supernatant was decanted, and the residue was washed twice with 30 mL of pentane/diethyl ether (3:1) at -30 °C. Because the residue still contained some unreacted 9a, it was redissolved in 20 mL of CH₂Cl₂ and cooled to -30 °C and an additional 25 μL of DMADC was added upon which the color of the solution immediately changed to yellow-brown. The solution was evaporated to dryness, and the crude product was purified by column chromatography on silica. Elution with diethyl ether/CH₂Cl₂ (2:1) afforded a light yellow fraction that was evaporated to dryness. The brownish-yellow residue was washed twice with 10 mL of diethyl ether/pentane (1:1) and dried in vacuo, yielding 2.2 g (4.4 mmol, 85%) of bright yellow product. Yellow crystalline needles were obtained by slow addition of THF to a suspension of 300 mg of 13a in 2.5 mL of diethyl ether until the product was completely dissolved, followed by cooling to -30 °C for several days.

Synthesis of Fe(CO)₃N(*t*-Bu)=C(H)—C(Me)C(CO₂-

CH₃)=C(CO₂CH₃)C(O)O (13b). A freshly prepared solution of 8 mmol of Fe(CO)₃(*t*-Bu—N=C(H)—C(Me)=O) (9b) in 80 mL of pentane (*vide supra*) was cooled to -78 °C under an atmosphere of CO, and a solution of 1 mL (8.1 mmol) of DMADC in 50 mL of pentane/diethyl ether (4:1) was added dropwise during ca. 45 min. During the reaction the intensely purple solution turned pale purple and the yellow-brown crude product precipitated. After the supernatant was decanted, the residue was washed twice with 30 mL of pentane/diethyl ether (3:1) at -30 °C and dried in vacuo. The residue was then redissolved in 5 mL of CH₂Cl₂ and purified by column chromatography on silica. Elution with diethyl ether/CH₂Cl₂ (2:1) gave a yellow-brown fraction that was evaporated to dryness. The residue was washed twice with 15 mL of pentane/diethyl ether (2:1) and once with 10 mL of diethyl ether and dried in vacuo, yielding ca. 2.3 g (5.3 mmol, 65%) of yellow product. Yellow-brown crystals suitable for X-ray diffraction were obtained by recrystallization as described for complex 13a.

Crystal Structure Determination and Refinement of 13b. The crystallographic data and numerical details for the complex 13b are listed in Table I. A brownish block shaped crystal was mounted on top of a glass fiber and transferred to an Enraf-Nonius CAD4 diffractometer for data collection at 100 K. Unit cell parameters were determined from a least squares treatment of the SET4 setting angles of 25 reflections with 14.0 < θ < 19.4°. The unit cell parameters were checked for the presence of higher lattice symmetry.¹⁶ Data were corrected for L_p and for a small linear decay (6.5%) of the intensity control reflections during the 43 h of X-ray exposure time but not for absorption. The structure was solved with standard Patterson methods (SHELXS86¹⁷) and a series of subsequent difference Fourier analyses. Refinement on F was carried out by full matrix least squares techniques. H atoms were introduced on 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 with one common isotropic thermal parameter (U = 0.022(2) Å²). Weights were

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Table I. Crystallographic Data and Details of Data Collection and Refinement for 13b

(a) Crystal Data	
formula	$\text{C}_{17}\text{H}_{19}\text{NO}_9\text{Fe}$
M_w	437.19
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
a, b, c (Å)	8.627(1), 9.597(2), 11.557(1)
α, β, γ (deg)	81.60(1), 88.75(1), 83.19(2)
V (Å ³), Z	939.8(2), 2
D_{calc} (g/cm ³)	1.545
$F(000)$	452
μ (cm ⁻¹)	8.5
cryst size (mm)	0.22 × 0.35 × 0.43
(b) Data Collection	
temp (K)	100
$\theta_{\text{min}}, \theta_{\text{max}}$	1.78, 29.38
radiation, λ (Å)	Mo K α (Zr-filtered), 0.710 73
scan type	$\omega/2\theta$
$\Delta\omega$ (deg)	0.60 + 0.35 tan θ
hor and vert aperture (mm)	3.0, 5.0
dist cryst to detector (mm)	173
ref reflns	130, 2, 0, -3, 013
data set	$h, -11$ to $+11$; $k, -12$ to $+12$; $l, -15$ to 0
total no. of data	5080
total no. of unique data	4835
no. of obsd data ($I > 2.5\sigma(I)$)	4165
(c) Refinement	
no. of refined params	272
weighting scheme	$w = 1.0/[\sigma^2(F) + 0.000423F^2]$
final R, R_w, S	0.0405, 0.0669, 1.07
$(\Delta/\sigma)_{\text{av}}$ in final cycle	0.038
res dens (min, max) (e Å ⁻³)	-0.70, 0.78

introduced in the final refinement cycles, and convergence was reached at $R = 0.0405$, $R_w = 0.0669$.

Neutral atom scattering factors were taken from Cromer and Mann (1968)¹⁸ and corrected for anomalous dispersion.¹⁹ All calculations were performed with SHELX76²⁰ and PLATON²¹ (geometrical calculations and illustrations) on a MicroVAX computer.

Results and Discussion

Formation of $\text{Fe}(\text{CO})_3(t\text{-Bu-N}=\text{C}(\text{H})-\text{C}(\text{R})=\text{O})$ (9a,b). The reaction of $\text{Fe}_2(\text{CO})_9$ with the α -imino ketones $t\text{-Bu-N}=\text{C}(\text{H})-\text{C}(\text{R})=\text{O}$ ($\text{R} = \text{Ph}, \text{CH}_3$) at room temperature in THF resulted in initial formation of purple $\text{Fe}(\text{CO})_3(t\text{-Bu-N}=\text{C}(\text{H})-\text{C}(\text{R})=\text{O})$ complexes (9a,b). The chelate $\sigma\text{-O}, \sigma\text{-N}$ -coordination mode of the heterodiene ligand in complexes 9a,b was confirmed by the IR and ¹H and ¹³C NMR spectroscopic data. It should be noted that the mononuclear complexes 9a,b are difficult to isolate and characterize, as they readily react further under the reaction conditions to form stable dinuclear complexes (*vide infra*). Analogous to the related $\text{Fe}(\text{CO})_3(\text{R}-\text{DAB})$ complexes,²² complexes 9a,b are intensely colored and highly air-sensitive. In the $\text{Fe}(\text{CO})_3(\text{R}-\text{DAB})$ complexes the intense color is the result of an electronic transition in the visible region of the Fe d-electrons (HOMO) to a delocalized π^* -orbital on the R-DAB ligand (LUMO). MO calculations and resonance Raman (rR) spectra have shown that in $\text{Fe}(\text{CO})_3(\text{R}-\text{DAB})$ these transitions hardly possess any charge transfer character due to the strongly mixed metal-d, ligand- π^* character of both the HOMO

and LUMO and therefore do not show solvatochromic behavior.²³ The presence of a similar transition in the $\text{Fe}(\text{CO})_3(t\text{-Bu-N}=\text{C}(\text{H})-\text{C}(\text{R})=\text{O})$ complexes (9a λ_{max} (pentane) = 535 nm, $\lambda_{\text{max}}(\text{THF}) = 538$ nm; 9b λ_{max} (pentane) = 518 nm, $\lambda_{\text{max}}(\text{THF}) = 519$ nm) indicates that the chelate-coordinated imino ketone possesses a similar delocalized π^* -orbital. This in turn implies that in complexes 9a,b the heterodiene ligand is bonded in a $\sigma\text{-N}, \sigma\text{-O}$ chelate fashion and adopts a planar-*syn* conformation in order to achieve maximum orbital overlap between the CN and CO chromophores. It has been shown that the conformational preference of the $\text{N}=\text{C}-\text{C}=\text{O}$ skeleton in general is the result of a balance between the conformation with minimal steric interaction of the skeleton substituents (nonplanar-*gauche* with an $\text{N}=\text{C}/\text{C}=\text{O}$ torsion angle of about 90°) and the conformation with maximum resonance stabilization by orbital overlap between the $\text{C}=\text{N}$ and $\text{C}=\text{O}$ chromophores (planar-*syn* or planar-*anti*).²⁴ On basis of the *gauche* conformation of the ligand skeleton observed in $\text{PhHC}(\text{Me})\text{N}=\text{C}(\text{Ph})-\text{C}(\text{Ph})=\text{O}$,²⁵ in monodentate N bonded *trans*-[PtCl₂(PR₃)(RN=C(H)-C(Me)=O)],¹¹ and in bidentate bridging bonded (AlMe₃)₂(σ, σ' -N,O-(MeN=C(Ph)-C(Ph)=O)),²⁶ van Vliet and co-workers concluded that in the case of the α -imino ketones the influence of the steric factors is predominant. The observed planar-*syn* conformation of the ligand in $\text{Fe}(\text{CO})_3(t\text{-Bu-N}=\text{C}(\text{H})-\text{C}(\text{R})=\text{O})$ suggests however that in chelate-coordinated α -imino ketones the orbital overlap of the chromophores is more important than minimizing the steric interaction between the skeleton substituents.

Reaction of Complexes 9a,b with $\text{Fe}(\text{CO})_n$ and Free Ligand. When the reaction mixture was stirred at room temperature for a prolonged period (> 1 h), the $\text{Fe}(\text{CO})_3(t\text{-Bu-N}=\text{C}(\text{H})-\text{C}(\text{R})=\text{O})$ complexes reacted with $\text{Fe}(\text{CO})_n$ fragments and free ligand in solution to form stable dinuclear species. If the reaction was carried out in a noncoordinating solvent (i.e. pentane) at room temperature, the reaction time increased significantly due to the reduced reactivity of $\text{Fe}_2(\text{CO})_9$, resulting in the formation of a larger percentage of dinuclear products. The $\text{Fe}(\text{CO})_3(t\text{-Bu-N}=\text{C}(\text{H})-\text{C}(\text{Me})=\text{O})$ complex (9b) readily reacted further under the reaction conditions and even removal of the solvent resulted in formation of an increased amount of two types of dinuclear products. Preliminary results (IR, ¹H NMR)²⁷ indicate that one of these products is structurally analogous to the $\text{Fe}_2(\text{CO})_6\text{L}$ complex 7 (Scheme II), formed in the reaction of the related α -imino ester $\text{PhCH}(\text{Me})\text{N}=\text{C}(\text{H})-\text{C}(\text{OEt})=\text{O}$ with $\text{Fe}_2(\text{CO})_9$ described by Weiss et al.^{13,14} The 1-aza-4-oxo-1,3-buta-

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(27) IR: ($\text{Fe}_2(\text{CO})_6\text{L}$, $\nu(\text{CO})$ in pentane) 2071 (s), 2019 (vs), 2001 (s), 1987 (s), 1960 (m), 1955 (m) cm^{-1} ($\text{R} = \text{Me}$); 2069 (s), 2019 (vs), 1999 (s), 1986 (s), 1962 (m), 1953 (m) cm^{-1} ($\text{R} = \text{Ph}$); ($\text{Fe}_2(\text{CO})_6(\text{L}-\text{L})$, $\nu(\text{CO})$ in CH_2Cl_2) 2005 (s), 1952 (m), 1922 (vs) cm^{-1} . ¹H NMR (CDCl_3 , 293 K, 300.13 MHz): ($\text{Fe}_2(\text{CO})_6\text{L}$ ($\text{R} = \text{Me}$)) δ 3.77 (s, 1H, CH=N), 1.86 (s, 3H, $\text{CH}_3\text{C}=\text{O}$), 1.58 (s, 9H, $(\text{CH}_3)_3\text{C}-\text{N}$); ($\text{Fe}_2(\text{CO})_6\text{L}$ ($\text{R} = \text{Ph}$)) δ 4.48 (s, 1H, CH=N), 7.35-7.57 (m, 5H, C_6H_5), 1.67 (s, 9H, $(\text{CH}_3)_3\text{C}-\text{N}$); ($\text{Fe}_2(\text{CO})_6(\text{L}-\text{L})$) ($\text{R} = \text{Me}$) δ 7.80 (s, 2H, CH=N), 1.38 (s, 6H, $\text{CH}_3\text{C}=\text{O}$), 1.39 (s, 18H, $(\text{CH}_3)_3\text{C}-\text{N}$).

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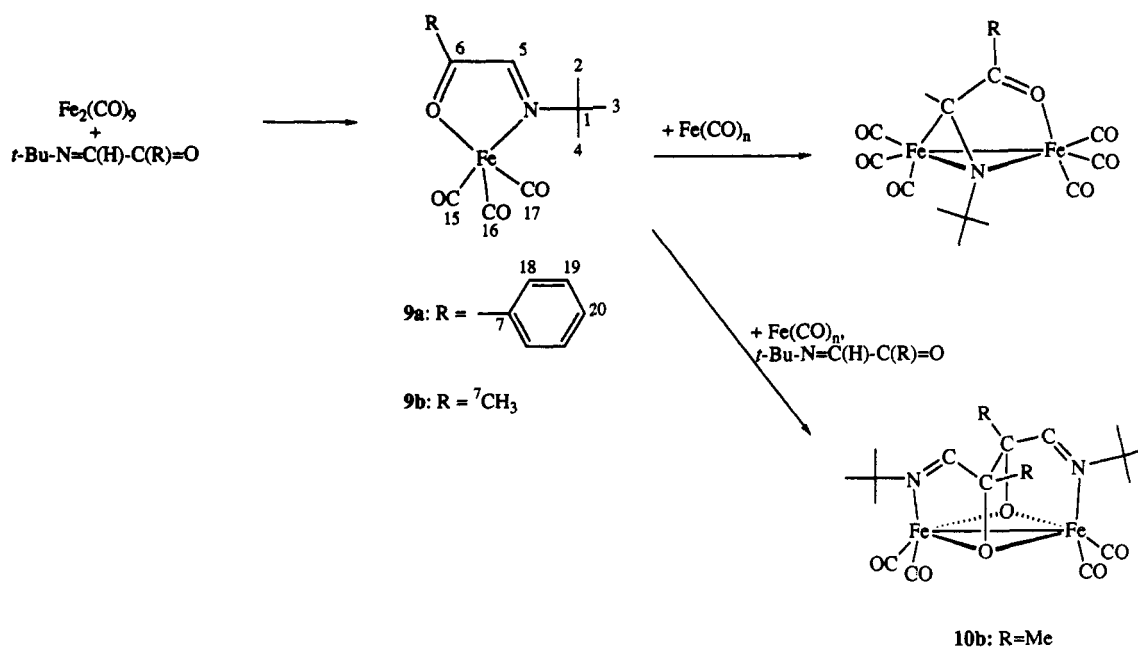
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Scheme III



diene ligand in $\text{Fe}_2(\text{CO})_6\text{L}$ is $\sigma\text{-O}$, $\mu^2\text{-N}$, $\eta^2\text{-C}=\text{N}$ coordinated to the two iron centers and donates 6 electrons, analogous to 1,4-diaza-1,3-butadienes in $\text{Fe}_2(\text{CO})_6(\text{R-DAB})$ complexes.²⁸ It should be noted that in these reactions a purple intermediate was observed to which the authors assigned a monodentate N-coordinated $\text{Fe}(\text{CO})_4(\text{imino ester})$ complex, but which in view of our findings is more likely to be the chelate tricarbonyl species. The second dinuclear product obtained after subsequent reaction of complex **9b** was identified, on the basis of the spectroscopic data,²⁷ as $\text{Fe}_2(\text{CO})_4(\text{L-L})$ (**10**) (Scheme III). In complex **10** two α -imino ketones are reductively coupled via the ketone carbon atoms. The newly formed ligand is formally dianionic and donates a total of 10 electrons to the two iron centers, 6 electrons from the two bridging oxygen atoms and 4 electrons from the two intact imine nitrogen atoms. The green $\text{Fe}_2(\text{CO})_4(\text{L-L})$ complex spectroscopically and structurally closely resembles the dinuclear C—C coupled diazabutadiene complex $\text{Ru}_2(\text{CO})_4(\text{R-ADA})$.²⁹ Reaction of the related α -imino ester with $\text{Fe}_2(\text{CO})_9$,^{13,14} apart from complex **7**, also resulted in formation of a dinuclear complex $\text{Fe}_2(\text{CO})_6(\text{L-L})$ (**8**) that contains two C—C coupled heterodiene ligands; in this complex however the two α -imino ketones are reductively coupled via the imine carbon atoms and the intact ketone moieties are not involved in coordination to the metal center.

In contrast to complex **9b**, the phenyl-substituted complex **9a** is relatively stable and only a small amount of $\text{Fe}_2(\text{CO})_6\text{L}$ (<5%) is formed during the reaction. This increase in stability compared to complex **9b** is probably due to the steric properties of the phenyl substituent, that hinder the $\text{Fe}(\text{CO})_n$ fragments in approaching the C=N bond (and therefore formation of $\text{Fe}_2(\text{CO})_6\text{L}$)³⁰ and block

the C—C coupling reaction of the ketone moieties that gives the $\text{Fe}_2(\text{CO})_4(\text{L-L})$ complex. The synthesis and complete characterization of the dinuclear complexes discussed above will be the subject of a forthcoming publication.³¹

Reaction of Complexes 9a,b with DMADC. The mononuclear $\text{Fe}(\text{CO})_3(t\text{-Bu-N}=\text{C}(\text{H})-\text{C}(\text{R})=\text{O})$ (R = Ph, Me) complexes react chemoselectively with 1 equiv of DMADC at -78°C in pentane under an atmosphere of CO to give the $\text{Fe}(\text{CO})_3$ (butenolide) complexes **13** in high yield (cf. Scheme IV). These complexes are obtained as purple-brown (**13a**) or yellow-brown precipitates (**13b**). Because the purple-brown precipitate of **13a** still contained some unreacted **9a**, it was dissolved in CH_2Cl_2 and an additional small amount of DMADC was added to ensure complete conversion (see Experimental Section). This difference in workup procedure combined with the observed increase in reaction time of phenyl substituted complex **9a** indicates a somewhat decreased reactivity of the latter complex toward the activated alkyne, which is probably due to the electron-withdrawing properties of the phenyl group (*vide infra*). The yellow air-stable Fe^0 complexes **13**, containing highly functionalized heterocyclic ligands, have been characterized by spectroscopic means and by elemental analyses. The proposed structure was confirmed by a single crystal X-ray diffraction analysis of complex **13b**. The five-membered butenolide heterocycle is formed through a series of metal-mediated C—C bond formations between a carbonyl ligand, the activated alkyne, and the ketone moiety of the former heterodiene ligand.

Molecular Structure of Complex 13b. An ORTEP drawing of the molecular structure of complex **13b** together with the atomic numbering is shown in Figure 1. The atomic coordinates and bond lengths and angles are given in Tables II and III. The coordination around the central iron atom is distorted trigonal bipyramidal with, as is expected for a $d^8\text{-tbp}$ complex,³² the imine nitrogen occupying an axial position and the C(8)—C(11) double bond in an equatorial position. A similar arrangement

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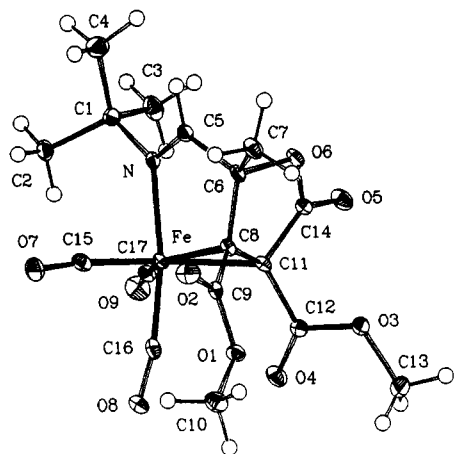


Figure 1. Thermal motion ellipsoid plot (at the 50% probability level) of complex 13b with the adopted atom labeling.

Table II. Fractional Coordinates of the Non-Hydrogen Atoms and Equivalent Isotropic Thermal Parameters of Complex 13b

atom	x	y	z	$U_{eq}, \text{Å}^2$ ^a
Fe	0.20166(4)	0.04598(4)	0.18478(3)	0.0100(1)
O(1)	0.2221(2)	0.3951(2)	0.08549(16)	0.0137(5)
O(2)	0.4676(2)	0.3034(2)	0.05084(18)	0.0197(6)
O(3)	0.0868(2)	0.4182(2)	0.34367(17)	0.0159(6)
O(4)	-0.0656(2)	0.3082(2)	0.24070(18)	0.0178(6)
O(5)	0.1867(2)	0.1489(2)	0.50740(17)	0.0196(6)
O(6)	0.4161(2)	0.1394(2)	0.41318(16)	0.0138(5)
O(7)	0.3346(3)	-0.0222(2)	-0.03997(18)	0.0224(6)
O(8)	-0.0195(2)	0.2064(2)	0.01358(18)	0.0212(6)
O(9)	-0.0699(2)	-0.1106(2)	0.25077(19)	0.0217(6)
N	0.3792(3)	-0.0880(2)	0.27120(19)	0.0115(6)
C(1)	0.3876(3)	-0.2479(3)	0.3014(2)	0.0145(7)
C(2)	0.3206(3)	-0.3111(3)	0.2017(2)	0.0165(8)
C(3)	0.2925(4)	-0.2748(3)	0.4138(3)	0.0206(8)
C(4)	0.5563(3)	-0.3172(3)	0.3226(3)	0.0245(9)
C(5)	0.4941(3)	-0.0268(3)	0.2968(2)	0.0128(7)
C(6)	0.4708(3)	0.1320(3)	0.2922(2)	0.0119(7)
C(7)	0.6212(3)	0.1993(3)	0.2764(3)	0.0169(8)
C(8)	0.3300(3)	0.2007(3)	0.2167(2)	0.0115(7)
C(9)	0.3513(3)	0.3036(3)	0.1107(2)	0.0126(7)
C(10)	0.2272(3)	0.4862(3)	-0.0266(3)	0.0193(8)
C(11)	0.1961(3)	0.1990(3)	0.2945(2)	0.0114(7)
C(12)	0.0564(3)	0.3117(3)	0.2874(2)	0.0118(7)
C(13)	-0.0416(3)	0.5314(3)	0.3440(3)	0.0208(8)
C(14)	0.2561(3)	0.1590(3)	0.4159(2)	0.0131(7)
C(15)	0.2869(3)	-0.0052(3)	0.0500(2)	0.0148(7)
C(16)	0.0641(3)	0.1535(3)	0.0868(2)	0.0144(7)
C(17)	0.0400(3)	-0.0567(3)	0.2308(2)	0.0144(7)

$${}^a U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

was observed in the solid state structure of the related $\text{Fe}(\text{CO})_3(1,5\text{-dihydropyrrol-2-one})$ complex (Figure 2).² The largest deviation from *tbp* geometry in 13b is observed for the N(1)-Fe-C(16) angle ($169.83(10)^\circ$), which is probably the result of a steric interaction forcing the axial carbonyl ligand to bend away from the bulky ester substituents on the C(8) and C(11) carbon atoms. The distortion in the geometry of the sp^3 -hybridized C(6) atom is likely to be the result of the axial/equatorial arrangement of N(1) and the C(8)-C(11) double bond (*vide supra*). The relatively short Fe-C(16) (1.784(3) Å) distance as compared to Fe-C(15) (1.816(2) Å) and Fe-C(17) (1.827(3) Å) reflects the trans influence of the σ -donating imine nitrogen, which

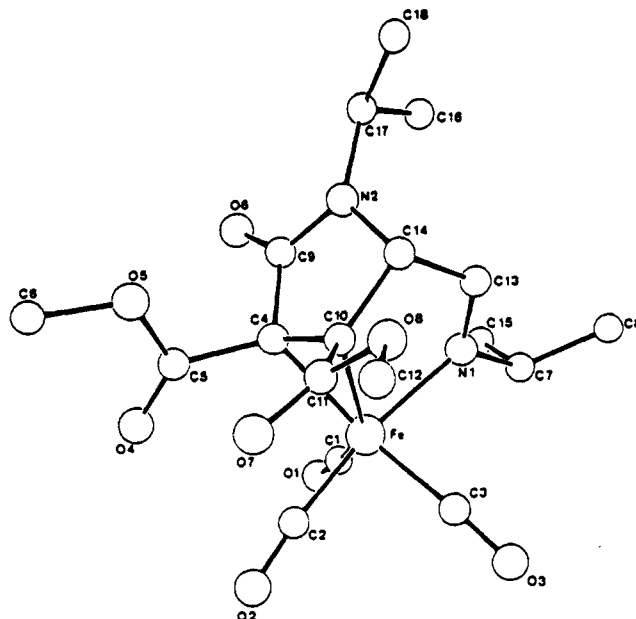


Figure 2. Molecular structure of $\text{Fe}(\text{CO})_3(1,5\text{-dihydropyrrol-2-one})$ (4) (after ref 2).

Table III. Bond Distances (Å) and Angles (deg) of the Non-Hydrogen Atoms of 13b (Esd's in Parentheses)

Fe-N	2.055(2)	O(3)-C(13)	1.457(3)	C(1)-C(2)	1.532(4)
Fe-C(8)	2.033(3)	O(4)-C(12)	1.199(3)	C(1)-C(3)	1.527(4)
Fe-C(11)	2.072(3)	O(5)-C(14)	1.201(3)	C(1)-C(4)	1.536(4)
Fe-C(15)	1.816(2)	O(6)-C(6)	1.475(3)	C(5)-C(6)	1.507(4)
Fe-C(16)	1.784(3)	O(6)-C(14)	1.371(3)	C(6)-C(7)	1.513(4)
Fe-C(17)	1.827(3)	O(7)-C(15)	1.137(3)	C(6)-C(8)	1.536(4)
O(1)-C(9)	1.344(3)	O(8)-C(16)	1.144(3)	C(8)-C(9)	1.480(4)
O(1)-C(10)	1.456(4)	O(9)-C(17)	1.136(3)	C(8)-C(11)	1.448(4)
O(2)-C(9)	1.206(3)	N-C(1)	1.517(3)	C(11)-C(12)	1.516(4)
O(3)-C(12)	1.342(3)	N-C(5)	1.272(4)	C(11)-C(14)	1.487(3)
N-Fe-C(8)	83.96(10)	O(6)-C(6)-C(7)	107.6(2)		
N-Fe-C(11)	95.44(9)	O(6)-C(6)-C(8)	104.0(2)		
N-Fe-C(15)	87.15(11)	C(5)-C(6)-C(7)	113.4(2)		
N-Fe-C(16)	169.83(10)	C(5)-C(6)-C(8)	112.0(2)		
N-Fe-C(17)	98.59(11)	C(7)-C(6)-C(8)	118.3(2)		
C(8)-Fe-C(11)	41.31(10)	Fe-C(8)-C(9)	108.67(19)		
C(8)-Fe-C(15)	102.85(11)	Fe-C(8)-C(11)	112.25(17)		
C(8)-Fe-C(16)	97.92(12)	Fe-C(8)-C(17)	70.76(16)		
C(8)-Fe-C(17)	147.17(11)	C(6)-C(8)-C(9)	120.5(2)		
C(11)-Fe-C(15)	143.01(12)	C(6)-C(8)-C(11)	105.8(2)		
C(11)-Fe-C(16)	92.48(12)	C(9)-C(8)-C(11)	127.3(2)		
C(11)-Fe-C(17)	106.12(11)	O(1)-C(9)-O(2)	123.4(2)		
C(15)-Fe-C(16)	82.69(12)	O(1)-C(9)-C(8)	111.8(2)		
C(15)-Fe-C(17)	109.96(12)	O(2)-C(9)-C(8)	124.8(3)		
C(16)-Fe-C(17)	85.28(12)	Fe-C(11)-C(8)	67.93(15)		
C(9)-O(1)-C(10)	114.55(19)	Fe-C(11)-C(12)	118.02(17)		
C(12)-O(3)-C(13)	114.5(2)	Fe-C(11)-C(14)	119.7(2)		
C(6)-O(6)-C(14)	109.73(18)	C(8)-C(11)-C(12)	125.5(2)		
Fe-N-C(1)	126.80(18)	C(8)-C(11)-C(14)	107.4(2)		
Fe-N-C(5)	114.32(17)	C(12)-C(11)-C(14)	112.0(2)		
C(1)-N-C(5)	118.8(2)	O(3)-C(12)-O(4)	123.6(3)		
N-C(1)-C(2)	110.4(2)	O(3)-C(12)-C(11)	110.0(2)		
N-C(1)-C(3)	105.7(2)	O(4)-C(12)-C(11)	126.3(3)		
N-C(1)-C(4)	111.8(2)	O(5)-C(14)-O(6)	120.7(2)		
C(2)-C(1)-C(3)	111.5(2)	O(5)-C(14)-C(11)	130.0(2)		
C(2)-C(1)-C(4)	108.0(2)	O(6)-C(14)-C(11)	109.3(2)		
C(3)-C(1)-C(4)	109.5(2)	Fe-C(15)-O(7)	172.3(2)		
N-C(5)-C(6)	118.2(2)	Fe-C(16)-O(8)	169.5(2)		
O(6)-C(6)-C(5)	98.99(19)	Fe-C(17)-O(9)	172.6(2)		

enhances π -back-donation to this carbonyl. The relatively short distance of the intact imine bond (N(1)-C(5) = 1.272(4) Å), which was also found in $[\text{PtCl}_2(\text{PBU}_3)_2](t\text{-Bu-DAB})$ ^{33a} and in $\text{Fe}(\text{CO})_3(1,5\text{-dihydropyrrol-2-one})$ (4), indicates that there is hardly any π -back-donation to this isolated imine fragment. The asymmetric coordination

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Table IV. IR Data and Elemental Analyses of Complexes 9 and 13

compd	IR ^a $\nu(\text{CO})$, cm ⁻¹	elemental anal. [obs (calc)]		
		C	H	N
9a	2047 (s), 1985 (s), 1956 (s) ^b	not analyzed		
9b	2043 (s), 1995 (s), 1928 (s) ^b	not analyzed		
13a	2060 (s), 2002 (sh), 1980 (s), 1765 (m), 1736 (m), 1708 (m) ^c	52.61 (52.93)	4.11 (4.24)	2.77 (2.81)
13b	2060 (s), 2001 (sh), 1978 (s), 1763 (m), 1736 (m), 1707 (m) ^c	46.71 (46.70)	4.51 (4.38)	3.26 (3.20)

^a s = strong, sh = shoulder, m = medium. ^b Measured in pentane. ^c Measured in THF.

Table V. ¹H NMR Data for Complexes 9 and 13

nucleus	δ values (multiplicity, ^a rel intens)			
	9a ^b	9b ^c	13a ^c	13b ^c
H(2),(3),(4)	1.78 (s, 9H)	1.38 (s, 9H)	1.38 (s, 9H)	1.38 (s, 9H)
H(5)	8.23 (s, 1H)	7.81 (s, 1H)	7.97 (s, 1H)	8.04 (s, 1H)
H(7)		2.17 (s, 3H)		1.89 (s, 3H)
H(10),(13)			3.67 (s, 3H)	3.67 (s, 3H)
			3.89 (s, 3H)	3.73 (s, 3H)
H(18),(19),(20)	7.85–7.95 (m, 2H) 7.33–7.40 (m, 3H)		7.39–7.43 (m, 5H)	

^a s = singlet, m = multiplet, and br = broad. ^b δ values (in ppm, relative to TMS) have been measured in CDCl₃ solution at 293 K and 100.1 MHz. ^c Measured at 300.13 MHz.

of the olefin bond in the equatorial plane (Fe–C(8) = 2.033(3) Å, Fe–C(11) = 2.072(3) Å) is more pronounced than in the comparable Fe(CO)₃(1,5-dihydropyrrol-2-one) complex (2.045(3) and 2.062(3) Å). It is not clear whether this has to be ascribed to the change in electronic properties, which accompanies the substitution of an N–R fragment for an oxygen atom, or to the different conformation of the ester moiety on C(8). The rather long alkene double bond C(8)–C(11) of 1.448(4) Å is certainly the result not only of the coordination to the iron center but also of the conjugation of this bond with the C(14)–O(5) double bond. This is corroborated by the relatively short C(11)–C(14) distance of 1.487(3) Å and the small deviation from coplanarity of the C(8)–C(11) and C(14)–O(5) bonds (dihedral angle: 177.5(3)°). The relatively short C(8)–C(9) distance (1.480(4) Å) and the dihedral angle of the C(8)–C(11) and C(9)–O(2) bonds (177.3(3)°) suggest furthermore that there is additional conjugation of the alkene double bond with the carbonyl of the ester substituent on C(8).

IR Spectroscopy. The $\nu(\text{CO})$ absorptions and the analytical data for complexes 9 and 13 are listed in Table IV. In both chelate Fe(CO)₃(*t*-Bu–N=C(H)–C(R)=O) complexes 9a and 9b, the three terminal CO ligands give rise to three separate absorption bands of equal intensity in the $\nu(\text{CO})$ region. The σ -coordination of both heteroatoms is expected to result in a decrease in the C=O and C=N stretching frequencies relative to those in the free ligand. The coordination of a ketone O-donor site, to both main-group elements (Zn, Al, B, Hg, etc.)^{24a,34} and to transition metals in higher oxidation states (Fe²⁺, Fe³⁺, Ru²⁺),³⁵ results in a substantial coordination shift ($\Delta\nu(\text{C}=\text{O}) = -50$ to -150 cm⁻¹), which is mainly attributed to σ -donation. The coordination shift of the imine stretching frequencies is less pronounced and usually amounts to ca. -15 cm⁻¹ (e.g. in *trans*-[PtCl₂(PR₃)(RN=C(H)–C(R)=O)] complexes¹¹ and in [PtCl₂(PR₃)₂(R–DAB)]³³). It should be noted that the C=N stretching band is generally much less intense than the respective $\nu(\text{CO})$ band, especially when the heteroatoms are coordinated to a metal. In the chelate Fe(CO)₃(*t*-Bu–N=C(H)–C(R)=O) complexes only one band of medium intensity is observed between 1400 and 1750 cm⁻¹ (9a, 1450 cm⁻¹; 9b, 1445 cm⁻¹), which we assign to the C=O stretching mode. The large coordination shift ($\Delta\nu(\text{C}=\text{O}) \approx -200$ cm⁻¹) indicates a

substantial reduction of the C–O bond order which, apart from σ -donation, is also attributed to extensive π -back-donation from the zerovalent metal to the antibonding C=O orbital.

The three terminal CO ligands in complexes 13 give rise to a characteristic absorption pattern in the $\nu(\text{CO})$ region, a sharp absorption at high frequency (2060 cm⁻¹), and two partially resolved absorptions at lower wavenumbers (1980–2000 cm⁻¹). Three separate absorptions are observed in the organic carbonyl region for both complexes (1705–1765 cm⁻¹). As a consequence of ring strain, the carbonyl stretching bands of unsaturated four- and five-membered lactones are generally observed at frequencies (1740–1770 cm⁻¹) higher than those of open chain ester carbonyl groups.³⁶ Therefore the absorption at 1765 cm⁻¹ is assigned to the lactone carbonyl and those at 1730 and 1705 cm⁻¹ are assigned to the former alkyne ester carbonyls.

¹H and ¹³C NMR Spectroscopy. Complexes 9. The ¹H and ¹³C NMR data for complexes 9a,b are listed in Tables V and VI, respectively; the atomic numbering is given in Scheme III. The chelate σ -N, σ -O-coordination mode of the heterodiene ligand in the Fe(CO)₃(*t*-Bu–N=C(H)–C(R)=O) complexes (9a,b) is expressed by both the ¹H and the ¹³C NMR data. The imine proton resonances of 9a and 9b, are observed as singlets at 8.23 and 7.81 ppm, respectively, and are shifted downfield by ca. 0.3 ppm relative to those in the free ligand, which supports the σ -coordination of the imine nitrogen. A comparable downfield coordination shift of the imine proton is observed in chelate ZnCl₂(*t*-Bu–N=C(H)–C(R)=O) (R = OMe, NEt₂)^{24a} and in *trans*-[PtCl₂(PR₃)(*t*-Bu–N=C(H)–C(R')=O)],¹¹ where the α -imino ketone is monodentate σ -N-coordinated. The position of the imine proton resonance furthermore excludes the possi-

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Table VI. ^{13}C NMR Data for Complexes 9 and 13

nucleus	9a ^a	9b ^a	13a ^b	13b ^b
C(1)	66.0	64.3	66.0	65.5
C(2),(3),(4)	33.5	32.6	30.6	30.6
C(5)	143.1	141.4	176.0	177.9
C(6)	173.5	178.2	94.2	91.2
C(7)	137.6	20.5	134.2	19.2
C(8),(11)			56.3	63.0
			79.3	71.7
C(9),(12),(14)			169.7	169.2
			169.8	171.1
			171.2	171.8
C(10),(13)			52.6	52.2
			53.2	53.7
C(15),(16),(17)	214.1	213.5	205.4	205.9
			206.8	208.0
			211.1	210.1
C(18),(19)	125.8		125.6	
	130.0		129.1	
C(20)	129.3		129.6	

^a δ values (in ppm, relative to TMS) have been measured in acetone-*d*₆ solution at 293 K and 75.47 MHz. ^b Measured in CDCl_3 .

bility of a π,π -coordinated ligand, as observed in (mono-1-aza-1,3-diene)iron tricarbonyl complexes,³⁷ since this type of coordination would result in an upfield shift of this resonance of at least 1–2 ppm. In both complexes the resonances of the ketone substituents are shifted upfield compared to the free ligand, which indicates that the oxygen atom is also involved in coordination to the metal center. It should be noted however that a change in the chemical shift of the ketone substituents was also observed for monodentate σ -N-coordinated *trans*-[PtCl₂(PR₃)(*t*-Bu-N=CH-C(Me)=O)] (R = Et, *i*-Pr, Ph) complexes.¹¹ In these complexes a downfield shift of the Me substituent resonances is caused by the rigid nonplanar *gauche* conformation of the heterodiene ligand, which forces the methyl group in a position above the coordination plane in close proximity of the metal. For complexes 9a and 9b, however, this type of monodentate σ -N-coordination is ruled out on basis of the IR spectra and the ^{13}C NMR data, which indicate a tricarbonyl species.

The ^{13}C NMR data for both $\text{Fe}(\text{CO})_3(t\text{-Bu}-\text{N}=\text{C}(\text{H})-\text{C}(\text{R})=\text{O})$ complexes (9a and 9b³⁸) firmly support the proposed chelate coordination mode of the heterodiene ligand. The three terminal carbonyl ligands in complexes 9a,b give rise to a single resonance at 214.1 and 213.5 ppm, respectively, which indicates that they rapidly interchange positions on the NMR time scale at 263 K. The imine carbon resonance (9a, 143.1 ppm; 9b, 141.4 ppm) of the coordinated N=C fragments are shifted ca. 12 ppm upfield in comparison to the free ligands as a result of π -back-donation in the delocalized LUMO of the heterodienes. A similar coordination shift is found for the imine carbon resonances in chelate $\text{Fe}(\text{CO})_3(\text{R}-\text{DAB})$ (R = *i*-Pr, *t*-Bu).³⁹ The somewhat larger upfield coordination shift observed

for the ketone carbon resonances in 9a,b ($\Delta\delta \approx 20$ ppm) not only supports the proposed σ -donating coordination of the ketone oxygen atom but also indicates that the chelate coordination exerts a larger effect on the electron density of the ketone carbon atom in comparison to the imine carbon atom.

Complexes 13. The ^1H and ^{13}C NMR data for complexes 13,b are also listed in Tables V and VI, respectively; the atomic numbering is given in Figure 1. The NMR data for the $\text{Fe}(\text{CO})_3$ (butenolide) complexes in solution are in agreement with the molecular structure in the solid state. The position of the imine proton resonances of complexes 13 indicate the presence of an unchanged N=CH fragment. In both complexes the inequivalent methoxy protons of the former alkyne give rise to two separate resonances in the expected region between 3.6 and 3.9 ppm. The ^{13}C NMR data for complexes 13a,b are comparable to those of the earlier reported $\text{Fe}(\text{CO})_3(1,5\text{-dihydropyrrol-2-one})$ complexes (4). The resonances of the imine carbon atoms C(5) in complexes 13a,b, observed at 176.0 and 177.9 ppm, respectively, are shifted downfield (ca. 30 ppm) in comparison to those in the chelate complexes 9a,b. This is probably caused by the strongly reduced π -back-donation to the LUMO of the isolated C=N fragment, which is confirmed by the relatively short C=N distance observed in the solid state structure of complex 13b (*vide supra*). Pronounced changes in chemical shift are as a matter of course observed for the carbon atoms directly involved in the C—C coupling reactions. In both complexes the resonance of the former ketone carbon atom C(6) is shifted upfield by ca. 80 ppm as a consequence of the change in hybridization (sp^2 to sp^3). The sp^2 carbon atoms C(8) and C(11) of the former alkyne resonate between 56 and 80 ppm, which is within the range usually observed for coordinated alkene carbon atoms.⁴⁰

Complex Formation. In order to explain the observed product formation a reaction mechanism is proposed (cf. Scheme IV), analogous to the one observed in the reaction of $\text{Fe}(\text{CO})_3(\text{R}-\text{DAB})$ with activated alkynes. In an earlier part of this series we have demonstrated the isolobal analogy between the Fe—N=C fragment and an azomethine ylide as a typical representative of a Huisgen 1,3-dipole.⁶ Likewise the Fe—O=C fragment is isolobally related to a carbonyl ylide. The initial step in the reaction can thus be described as a 1,3-dipolar cycloaddition of dimethyl acetylenedicarboxylate to the Fe—O=C fragment, resulting in the formation of the bicyclo[2.2.1] intermediate 11. The relatively high yields and the absence of side products arising from Fe—N=C cycloaddition confirm that this initial step proceeds with complete chemoselectivity, which will be discussed later in more detail. Due to the high nucleophilicity of the coordinated oxygen atom, intermediate 11 rapidly undergoes a CO migration/insertion reaction in the Fe—O bond, resulting in the formation of a coordinatively unsaturated species. The latter intermediate takes up an additional ligand, which gives rise to the formation of the bicyclo[2.2.2] intermediate 12. In contrast to the bicyclo[2.2.2] complexes (Scheme I, complex 3) formed in the reactions of $\text{Fe}(\text{CO})_3(\text{R}-\text{DAB})$ with DMADC, intermediate 12 could not be detected spectroscopically because the reductive elimination and C—C coupling of the two Fe—C bonds

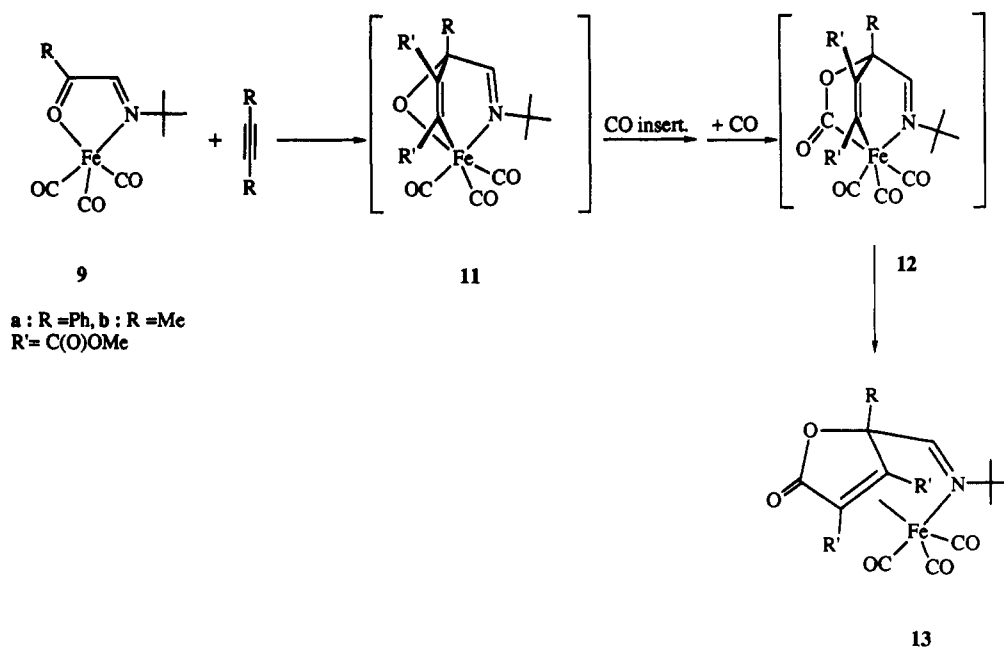
(37) (a) de Cian, A.; Weiss, R. E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* 1972, B28, 3264. (b) Otsuka, S.; Yoshida, T.; Nakamura, A. *Inorg. Chem.* 1967, 6, 20.

(38) While, due to the instability of complex 9b under the reaction conditions and during workup procedures, it was not possible to prepare a suitable ^{13}C NMR sample directly from the reaction mixture, an alternative procedure was used to obtain a pure sample of complex 9b. A solution of ca. 80 mg of $\text{Fe}_2(\text{CO})_4(\text{L}-\text{L})$ (10) in 2.5 mL of acetone-*d*₆ was placed in a HP-NMR tube and kept at 313 K for ca. 5 h under an atmosphere of 35 bar of CO. This resulted in a complete conversion of the dinuclear starting complex to the purple $\text{Fe}(\text{CO})_3(t\text{-Bu}-\text{N}=\text{C}(\text{H})-\text{C}(\text{Me})=\text{O})$ (9b).

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Scheme IV



forming the final product 13 proceed very fast at low temperature. When, in order to stabilize intermediate 12, $\text{P}(\text{OMe})_3$ was offered instead of CO as the additional ligand, the $\text{Fe}(\text{CO})_2(\text{P}(\text{OMe})_3)(\text{butenolide})$ complex was obtained, indicating that despite the presence of a good σ -donor, complex 12 still readily isomerizes. The instability of intermediate 12 in comparison to most of the R-DAB derived bicyclo[2.2.2] complexes 3 is tentatively attributed to the following factors: (a) the substitution of the more electronegative oxygen atom in the $\text{Fe}-\text{C}(\text{O})-\text{X}$ fragment ($\text{X} = \text{N}, \text{O}$), which probably weakens the relevant donative $\text{Fe}-\text{C}$ bond (in the Me as well as in the Ph substituted complex) and (b) methyl substitution at the bridgehead carbon atom, which favors reductive elimination, as is evident from the reactions of the biacetyl derived $\text{Fe}(\text{CO})_3(\text{R}-\text{DAB})$ complexes⁵ that also exhibit a very fast reductive elimination step.

Initial 1,3-Dipolar Cycloaddition; Reaction Rates and Chemoselectivity. By using the isolobal analogy, the organometallic $\text{Fe}-\text{X}=\text{C}$ dipoles ($\text{X} = \text{N}, \text{O}$) can be qualitatively compared with the classical organic 1,3-dipoles azomethine and carbonyl ylide. These organic ylides are termed nucleophilic or type I 1,3-dipoles (according to the Sustmann classification⁴¹), which implies that they possess relatively high lying frontier orbitals and react preferentially with electron deficient dipolarophiles. Cycloaddition reactions of this type of 1,3-dipole are HOMO-controlled; i.e., the interaction of the dipole HOMO with the dipolarophile LUMO is predominant. For the HOMO-controlled cycloadditions, both a decrease in the HOMO-LUMO gap, which is associated with an increase in diradical character,⁴² and a rise in the energy level of the HOMO will accelerate the reaction. Due to the presence of the more electronegative central oxygen atom, the carbonyl ylide possesses a smaller HOMO-

LUMO gap and therefore an increased reactivity in comparison to the azomethine ylide. On the basis of the preceding remarks, the organometallic cycloaddition reaction is also expected to be HOMO-controlled and the observed chemoselectivity can to some extent be rationalized (*vide infra*). It should be emphasized, however, that the two types of dipoles present in the $\text{Fe}(\text{CO})_3(\text{imino ketone})$ complex can hardly be regarded as two separate entities (the proposed *syn* configuration of the ligand implies a maximum orbital overlap of the $\text{C}=\text{O}$ and $\text{C}=\text{N}$ chromophores).

Houk et al. have demonstrated that substituents, on both the dipole and the dipolarophile, significantly change the frontier molecular orbital energies and coefficients and therefore can have a large influence on the relative rate and regioselectivity of the organic cycloaddition reaction.⁴³ For the HOMO-controlled cycloaddition, the substitution of an electron-withdrawing group on a terminus of the 1,3-dipole will lower the level of the HOMO and thus lead to a decrease in the reaction rate. This is observed for the present organometallic cycloaddition reaction; in 9a, with the phenyl substituent on the ketone carbon atom, the reaction is clearly more sluggish than in 9b.

Dedieu and co-workers have performed theoretical CAS-SCF calculations on both the model compound $\text{Fe}(\text{CO})_3(\text{HN}=\text{C}(\text{H})-\text{C}(\text{H})=\text{O})$ and the parent azomethine and carbonyl ylides.⁴⁴ These calculations indicate that the HOMO of the $\text{Fe}(\text{CO})_3(\text{imino ketone})$ system is found at slightly higher energy than those of the organic ylides and

(42) Theoretical studies indicate that 1,3-dipoles can, apart from the zwitterionic VB structures, also be described in terms of a spin-paired 1,3-diradical structure. The larger the contribution of the diradical structure to the wave function the more diradical character a 1,3-dipole possesses. In terms of MO's, the diradical character can be seen as a depopulation of the HOMO to the benefit of the LUMO. A decrease in the HOMO-LUMO gap leads to increasing degeneracy of the HOMO and the LUMO (more configuration interaction) and therefore an increase in diradical character. Houk, K. N.; Yamaguchi, K. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed., John Wiley and Sons Inc.: New York, 1984; Chapter 13.

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(41) Application of the frontier molecular orbital theory to 1,3-dipolar cycloadditions by Sustmann provides a semiquantitative classification of these cycloadditions into three types depending on the relative disposition of the 1,3-dipole and the dipolarophile frontier orbitals. (a) Sustmann, R. *Tetrahedron Lett.* 1971, 2717. (b) Sustmann, R.; Trill, H. *Angew. Chem., Int. Ed. Engl.* 1972, 11, 838. (c) Sustmann, R. *Pure Appl. Chem.* 1974, 40, 569.

that the HOMO-LUMO gap is smaller (i.e. more diradical character), which supports the proposed HOMO control for the organometallic cycloaddition with electrophilic alkynes. This may also explain the very low activation energies observed for the organometallic cycloadditions in comparison to their organic counterparts.

From the observed chemoselectivity one might conclude that, despite the charge delocalization over the whole metallacycle, the ketone carbon atom has a larger HOMO coefficient than the imine carbon atom. This has not been confirmed by the CAS-SCF calculations for the $Fe(CO)_3(HN=C(H)-C(H)=O)$ system in its most stable geometry. However, the same calculations on a geometrical isomer that is only slightly higher in energy (1.9 kcal/mol) do show an increased weight of the $Fe-O=C$ terminus in the HOMO.

In the previous discussion we have focused on the electronic influences governing the reaction rate and the chemoselectivity of the organometallic cycloaddition but we recognize that steric influences may also play an important role. On grounds of steric constraint it might be argued that the $Fe-O=C$ fragment is easier accessible due to the absence of a bulky substituent on the hetero-

(44) The CAS-SCF (complete active space self-consistent field) method is a particular case of the MC-SCF (multiconfiguration self-consistent field) method. In the MS-SCF method the wave function Ψ is expanded over electronic configurations Φ_i , i.e., $\Psi = \sum C_i \Phi_i$, and in the variation process both the coefficients C_i of the expansion and the electronic configurations Φ_i (or more precisely the orbitals on which the Φ_i 's are built) are optimized (see: Salahub, D. R.; Zerner, M. C. *The challenge of d- and f-electrons*; ACS Symposium Series 394; American Chemical Society: Washington, DC, 1989). The CAS-SCF calculations were performed by M. J. Liddell and A. Dedieu, University Louis Pasteur, Strasbourg, and will be published in a forthcoming paper.

atom. However this is not likely to be the main cause for the observed complete chemoselectivity since the *tert*-butyl substituted $Fe-N=C$ fragment in $Fe(CO)_3(t-Bu-DAB)$ has also been shown to readily react with DMADC.⁴⁵

Finally, one should bear in mind that the above remarks concerning the chemoselectivity and reaction rates are largely based on the comparison with the organic cycloadditions. The influence of the metal d-orbitals on the charge distribution in the 1,3-dipole, the reaction rates, and chemoselectivity have, to our knowledge, hardly been studied. In order to better understand the factors influencing the organometallic cycloadditions, further research on other metal systems and additional theoretical calculations are indispensable.

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Supplementary Material Available: A diagram of the compound and tables of fractional coordinates of the hydrogen atoms, anisotropic temperature factors, and complete bond distances and angles of the non-hydrogen atoms (5 pages). Ordering information is given on any current masthead page. A list of observed and calculated structure factors (28 pages) of complex **13b** can on request be obtained from the authors.

OM980233H

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