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Selective Coupling of an α-Diimine Ligand and CO and Methyl Propynoate Molecules To Give $Fe_2(CO)_n\{(R)N{=}C(H)C(H)N(R)C(O)C(H){=}CC(O)OMe\}$, Containing a Flyover-Type Ligand and Showing a Reversible CO-Induced Metal–Metal Bond Fission with X-ray Crystal Structures (n = 5, R = *i*-Pr; n = 6, R = c-Hex)[1]

Fred Muller, Gerard van Koten, and Kees Vrieze*

Laboratorium voor Anorganische Chemie, University of Amsterdam, J. H. van't Hoff Institute, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Dick Heijdenrijk

Laboratorium voor Kristallografie, University of Amsterdam, J. H. van't Hoff Institute, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

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Reaction of $Fe_2(CO)_6$(R-DAB) (**1a**, R = *i*-Pr; **1b**, R = c-Hex) with methyl propynoate at 20 °C in hexane solution yields a mixture of compounds of which two of the major products are the complexes $Fe_2(CO)_5\{RN{=}C(H)C(H)N(R)C(O)C(H){=}CC(O)OMe\}$ (**6**) and $Fe_2(CO)_6\{(R)N{=}C(H)C(H)N(R)C(O)C(H){=}CC(O)OMe\}$ (**7**). Both complexes contain an 8e-donating flyover-type ligand, resulting from the C–N coupling of an imine group of the α-diimine ligand and a CO, which is C–C coupled to a methyl propynoate molecule. The complexes are structurally similar to and isoelectronic with the known dinuclear iron carbonyl complexes with a flyover ligand resulting from the coupling of two alkynes and a CO. The X-ray crystal structures of **6b** (R = c-Hex) and **7a** (R = *i*-Pr) have been determined. Crystals of **6b**, $Fe_2C_{24}H_{28}N_2O_8$, are monoclinic, space group $P2_1/n$, and have cell constants a = 20.979 (2) Å, b = 8.9658 (8) Å, c = 14.963 (1) Å, β = 107.393 (9)°, and Z = 4. A total of 1034 absorption-corrected reflections (Cu Kα, μ = 92.8 cm^{-1}) have been used in the refinement resulting in a final R value of 0.077. Crystals of **7a**, $Fe_2C_{19}H_{20}N_2O_9$, are orthorhombic, space group $P2_12_12_1$, and have cell constants a = 14.1574 (16) Å, b = 16.0933 (10) Å, c = 10.2645 (9) Å, and Z = 4. A total of 1187 absorption-corrected reflections (Cu Kα, μ = 104.4 cm^{-1}) have been used in the refinement resulting in a final R value of 0.066 (R_w = 0.091). It is suggested that compound **6** is formed via the substitution of the η^2-C=N-coordinated imine moiety of the R-DAB in **1** by the η^2-coordinated alkyne, followed by the intramolecular coupling of the alkyne to one of the CO ligands. The resulting μ_2-C(R)=C(H)C(O) fragment, after the recoordination of one of the R-DAB C=N moieties, finally inserts in the Fe–N bond to give **6**. In the resulting compound the $Fe_2(CO)_5$ core (the Fe–Fe distance is 2.632 (4) Å, all CO's are terminally bonded) is bridged by the 8e-donating flyover ligand. Compound **6** reacts with CO to give **7** quantitatively. In the latter complex a CO is added to the $Fe(CO)_2$ unit in **6** and the Fe–Fe bond is broken (the Fe–Fe distance is 3.561 (4) Å, all CO's are terminally bonded). The geometry of the flyover ligand is hardly affected by this conversion. Upon heating a solution of **7** while purging it with N_2, one CO ligand is expelled and the Fe–Fe bond restored to give **6** again. The ^{1}H and ^{13}C NMR data of the reported compounds are in agreement with their molecular structure in the solid state.

Introduction

A fascinating aspect of the chemistry of transition-metal α-diimine complexes is the ease with which the coordinated α-diimine ligand may participate not only in C–H[2] and N–H[3] bond formation but also in C–C and N–C coupling reactions with a wide variety of unsaturated organic substrates, e.g. α-diimines,[4-8] carbodiimides (RN=C=NR),[9] sulfines ($R_2C{=}S{=}O$),[9] ketene ($H_2C{=}C{=}O$),[10] and alkynes (R′C≡CR″).[11] Of these reactions those involving $Ru_2(CO)_6$(R-DAB) [R-DAB = 1,4-diaza-1,3-butadiene; RN=C(H)C(H)=NR] containing a 6e-donating σ-N, μ_2-N′, η^2-C=N′ α-diimine ligand have been studied extensively. It has become clear now that in the case of reactions of $Ru_2(CO)_6$(R-DAB) C–C bond formation between one of the unsaturated C atoms of the organic substrate and the C atom of the η^2-C=N′ bonded moiety of the R-DAB ligand is the predominant reaction.

In order to investigate in more depth the influence of the nature of the metal and the ligands on these coupling reactions, we directed our attention to a detailed study of reactions of the homo- and heterodinuclear $M_2(CO)_6$(α-diimine) complexes [M_2 = Fe_2, FeRu, Ru_2; α-diimine = R-DAB, R-Pyca (= pyridine-2-carbaldimine)] with a variety of alkynes.

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* To whom correspondence should be addressed.

[1] Reactions of Dinuclear Metal Carbonyl α-Diimine Complexes with alkynes. 2. Part 1: see ref 30.

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Recently we reported some preliminary results on the reactions of $Fe_2(CO)_6$(R-DAB)[12] with methyl propynoate.[13] The products of these reactions are strikingly different from those of the reactions of $Ru_2(CO)_6$(R-DAB) with alkynes, since in the case of the Fe complex the R-DAB N atoms are involved in N–C bond formation, whereas in the case of the Ru complexes as yet no N–C coupling with alkynes has been observed. One of these products, $Fe_2(CO)_5$\{(R)N=C(H)C(H)N(R)C(O)C(H)=CC(O)OMe\} (**6**), shows a striking structural similarity to the well-known flyover bridge containing metal carbonyl complexes, e.g. $Fe_2(CO)_6$[C(Me)=C(Me)C(O)C(Me)=C(Me)],[14] which are frequently encountered as products of reactions of alkynes with both Fe and Ru carbonyl clusters.[15] Complex **6** shows a reversible reaction with CO at room temperature to give $Fe_2(CO)_6$\{(R)N=C(H)C(H)N(R)C(O)C(H)=CC(O)OMe\} (**7**), which contains the same flyover-type ligand but has no Fe–Fe bond anymore. Full details concerning the synthesis of these compounds as well as their structure and reactivity are reported in this paper.

Experimental Section

Materials and Apparatus. ^1H and ^{13}C NMR spectra were recorded on Bruker AC100 and WM250 spectrometers. IR spectra were measured with a Perkin-Elmer 283 spectrometer. Field-desorption (FD) mass spectra (FD-MS) were obtained on a Varian MAT711 double-focusing mass spectrometer, fitted with a 10-μm tungsten wire FD emitter containing carbon microneedles with an average length of 30 μm, using emitter currents of 0–10 mA. Elemental analyses were carried out by the section Elemental Analysis of the Institute for Applied Chemistry, TNO, Zeist, The Netherlands.

All preparations were carried out in an atmosphere of purified nitrogen, using carefully dried solvents. All column chromatography was performed by using silica gel (60 mesh, dried and activated before use) as the stationary phase. $Fe_2(CO)_6$(R-DAB) (R = *i*-Pr, c-Hex) was prepared according to known procedures.[7] Methyl propynoate and CO were used as commercially obtained.

Synthesis of $Fe_2(CO)_n$\{(R)N=C(H)C(H)N(R)C(O)C(H)=CC(O)OMe\} (6, n = 5; 7, n = 6; a, R = *i*-Pr; b, R = c-Hex). $Fe_2(CO)_6$(R-DAB) (**1a**, R = *i*-Pr, **1b**, R = c-Hex) (2 mmol, 840 mg (**1a**), 1000 mg (**1b**)) and methyl propynoate (6 mmol, 504 mg) were stirred in 50 mL of hexane at 20 °C for 24 h. The solvent and the excess of alkyne were evaporated, and the crude reaction mixture was dissolved in 5 mL of CH_2Cl_2 and separated by column chromatography. Elution with hexane afforded a small amount of $Fe(CO)_3$(R-DAB).[16] The next fraction (hexane/diethyl ether (9:1)) contained a minor amount of an as yet unidentified yellow product. Elution with hexane/diethyl ether (5:1) yielded a mixture of **6** and **7** with a total yield varying from 40 to 60% (based on **1**). Further elution with hexane/diethyl ether (1:1) and hexane/diethyl ether (1:3) produced the yellow complex $Fe_2(CO)_6$[(R)NC(H)C(H)N(R)C(H)CC(O)OMe] (yield 30%) and a minor amount of the blue complex $Fe_2(CO)_5$(R-DAB)[μ_2-HC=C(C(O)OMe)C(O)], respectively.[17] The composition of the mixture of **6** and **7** in the various preparations varied from 25:75 **6**/**7** to 80:20 **6**/**7**. Attempts to separate both products by further chromatography were not successful. Recrystallization of the mixture from a hexane/diethyl ether (9:1) solution yielded at −20 °C orange, air-stable crystals of **7** and at −80 °C brown, air-stable crystals, of **6**. IR (ν(CO)), FD-MS and elemental analysis data are listed in Table I.

Table I. IR (ν(CO)), Field-Desorption (FD-MS), and Elemental Analysis Data of $Fe_2(CO)_n$\{(R)N=C(H)C(H)N(R)C(O)C(H)=CC(O)OMe\} (6a; n = 5, R = *i*-Pr; 6b, n = 5, R = c-Hex; 7a, n = 6, R = *i*-Pr; 7b, n = 6, R = c-Hex)

compd	IR[a]	FD-MS[b,c]	elemental anal.[b]		
6a	2050 (s)	504	C	42.03	(42.89)
	2010 (s)	(504.06)	H	3.97	(4.00)
	1999 (w)		N	5.61	(5.56)
	1969 (s)				
	1951 (s)				
	1729 (m)				
	1680 (w)				
6b	2049 (s)	584	C	49.20	(49.34)
	2009 (s)	(584.18)	H	4.83	(4.83)
	1997 (w)		N	4.61	(4.80)
	1969 (s)				
	1950 (s)				
	1727 (m)				
	1680 (w)				
7a	2079 (s)	532	C	42.89	(42.89)
	2031 (s)	(532.07)	H	3.79	(3.79)
	1975 (s)		N	5.09	(5.26)
	1952 (s)				
	1730 (m)				
	1687 (m)				
7b	2076 (s)	612	C	48.38	(49.03)
	2030 (s)	(612.19)	H	4.50	(4.61)
	1969 (s)		N	4.32	(4.58)
	1950 (s)				
	1727 (m)				
	1685 (m)				

[a] In hexane solution, values in cm^{-1}. [b] Calculated values in parentheses. [c] Based on ^{57}Fe.

Reaction of 6 with CO To Give 7. A gentle stream of CO was bubbled through a solution of **6** (0.5 mmol) in 100 mL of hexane at 20 °C. The brown color slowly changed to orange, and a dark yellow microcrystalline solid precipitated. The conversion, which was virtually quantitative, was completed when in the IR spectrum the bands of **6** were replaced by those due to **7** after about half an hour. Complete precipitation of **7** was achieved by cooling the reaction mixture to −80 °C. This method can also be applied to obtain a pure sample of **7** from the mixture of **6** and **7** resulting from chromatography of the crude product of the reaction of $Fe_2(CO)_6$(R-DAB) with methyl propynoate. In this case CO is bubbled through the solution as obtained after chromatography. After completion of the conversion **7** is precipitated by cooling the solution to −80 °C.

Thermal Conversion of 7 to 6. In 100 mL of hexane, 1 mmol of **7** was heated to 60 °C, while a strong stream of N_2 was passed through the solution. In the IR spectrum of the reaction mixture the bands of **7** had disappeared after about half an hour, indicating that the conversion was complete. The brown reaction mixture was evaporated to dryness and the crude product purified by column chromatography. The product (**6**) was obtained by elution with hexane/diethyl ether (5:1) in a yield varying from 50 to 70%. This method can be used to obtain a pure sample of **6** from its mixture with **7** resulting from the reaction of $Fe_2(CO)_6$(R-DAB) with methyl propynoate.

Crystal Structure Determinations of 6b and 7a. The crystal, data aquisition, and refinement data are summarized in Table II. The reflections were measured at 25 °C on a Nonius CAD4 diffractometer using the θ–2θ scan method. The reflections with $I < 2.5\sigma(I)$ were treated as unobserved. The structures were solved by means of the heavy-atom method. The Fe atoms were located by using the symbolic addition program set SIMPEL.[18] The C, N, and O atomic positions were derived from a ΔF Fourier

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(17) The structure of $Fe_2(CO)_6$\{(R)NC(H)C(H)N(R)C(H)CC(O)OMe\}, containing a heterocyclic ligand resulting from the coupling of both R-DAB N atoms to the unsubstituted alkyne C atom of the methyl propynoate, was communicated recently.[13] The blue complex $Fe_2(CO)_5$(*i*-Pr-DAB)[μ_2-HC=C(C(O)OMe)C(O)] will be discussed in part 5 of this series.[28]

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Table II. Crystallographic Data for $Fe_2(CO)_5\{(c\text{-}Hex)N{=}C(H)C(H)N(c\text{-}Hex)C(O)C(H){=}CC(O)OMe\}$ (6b) and $Fe_2(CO)_6\{(i\text{-}Pr)N{=}C(H)C(H)N(i\text{-}Pr)C(O)C(H){=}CC(O)OMe\}$ (7a)

	6b	7a
formula; mol wt	$Fe_2C_{24}H_{28}N_2O_8$, 584.18	$Fe_2C_{19}H_{20}N_2O_9$, 532.07
space group	$P2_1/n$	$P2_12_12_1$
a, Å	20.979 (2)	14.1574 (16)
b, Å	8.9658 (8)	16.0933 (10)
c, Å	14.963 (1)	10.2645 (9)
α, deg	90	90
β, deg	107.393 (9)	90
γ, deg	90	90
V, $Å^3$	2637.2	233.7
d_{calcd}, $g{\cdot}cm^{-1}$; Z	1.47; 4	1.51; 4
μ, cm^{-1}	92.8	104.4
cryst color; size, mm^3	brown; 0.10 × 0.05 × 0.38	dark orange; 0.30 × 0.38 × 0.15
radiatn	Cu Kα, λ = 1.5418 Å	Cu Kα, λ = 1.5418 Å
2θ range, deg	6.5–100	5.0–130
no. of reflctns	2935	2284
no. with $I < 2.5\sigma(I)$	1901	1097
no. of reflctn in refinement	1034	1187
h min, max	−20, 20	−14, 14
k min, max	−8, 8	−3, 17
l min,max	0, 14	−10, 10
absorptn corr	DIFABS	DIFABS
extinctn corr	no	no
weighting scheme	units	$w = 1/(9.62 + F_o + 0.0085F_o^2)$
anomalous scattering	Fe	Fe
final R, R_w	0.077, ...	0.066, 0.109

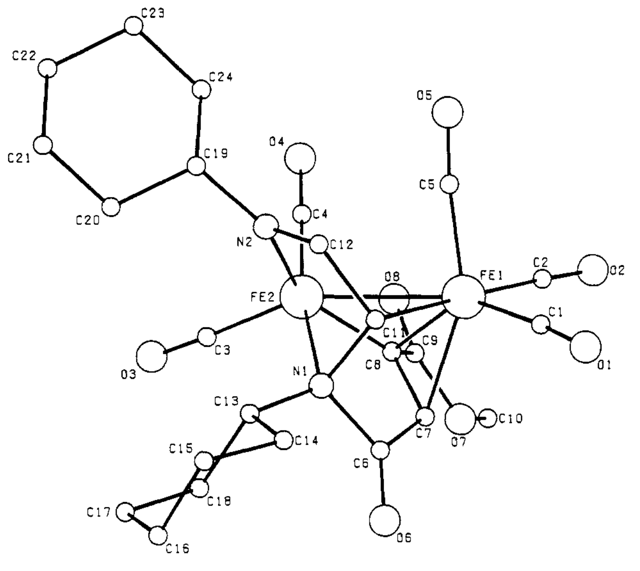
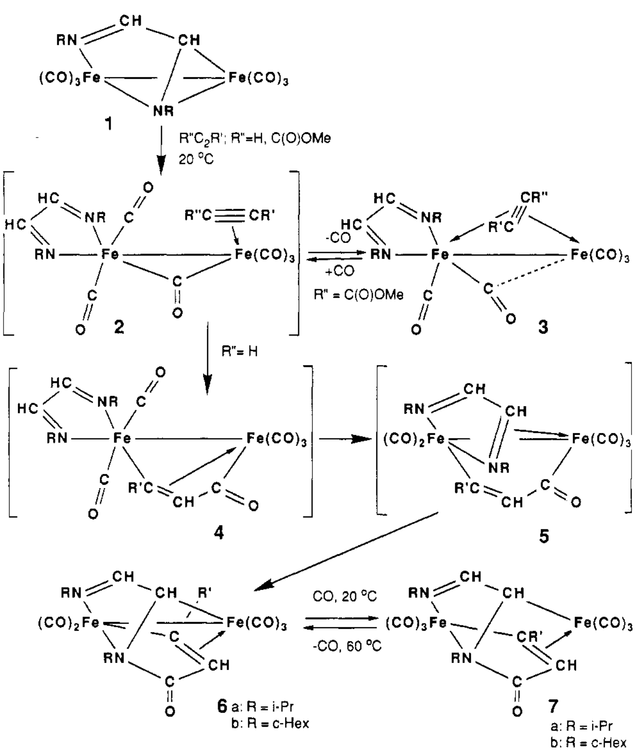


Figure 1. PLUTO drawing of **6b**. The H atoms are omitted for clarity.

Scheme I. Formation of 6 and 7 [a, R = *i*-Pr; b, R = *c*-Hex; R′ = C(O)OMe][a]



[a] The structures between brackets are proposed intermediates.

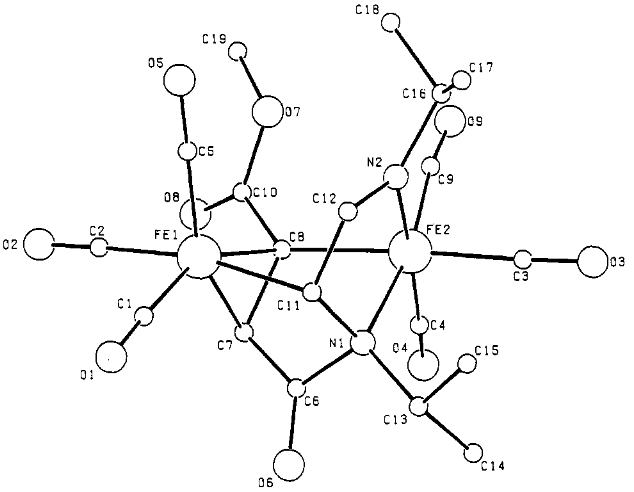


Figure 2. PLUTO drawing of **7a**. The H atoms are omitted for clarity.

synthesis. The positions of the H atoms of both **6b** and **7a** were calculated and were not refined. The non-hydrogen atoms of **7a** were further refined anisotropically, using block-diagonal least-squares calculations. The C, N, and O atoms of **6b** were refined isotropically and the Fe atoms anisotropically. The refinement in the presented enantiomeric crystal form of **7a** converged to $R = 0.066$ ($R_w = 0.109$), while for the other enantiomer the final residuals were $R = 0.071$ ($R_w = 0.113$), pointing to the former to be the right enantiomer. An empirical absorption correction (DIFABS)[19] was applied. The calculations were performed with XRAY76,[20] the atomic scattering factors were taken from Cromer and Mann (1968),[21] and the dispersion correction factors from ref 22.

Results and Discussion

$Fe_2(CO)_6$(R-DAB) (**1a**, R = *i*-Pr; **1b**, R = c-Hex) reacts at room temperature with methyl propynoate to give $Fe_2(CO)_5\{(R)N{=}C(H)C(H)N(R)C(O)C(H){=}CC(O)OMe\}$ (**6a**, R = *i*-Pr; **6b**, R = c-Hex) (among other products, see Experimental Section) which reacts with CO to give $Fe_2(CO)_6\{(R)N{=}C(H)C(H)N(R)C(O)C(H){=}CC(O)OMe\}$ (**7a**, R = *i*-Pr; **7b**, R = c-Hex). This latter complex loses a CO

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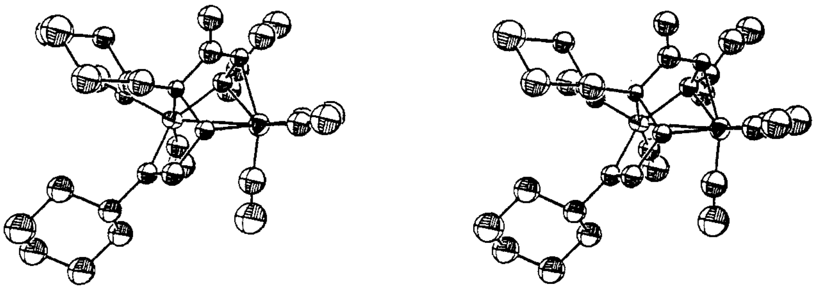


Figure 3. Stereospecific ORTEP representation of **6b** (ellipsoid probability scale: 30%).

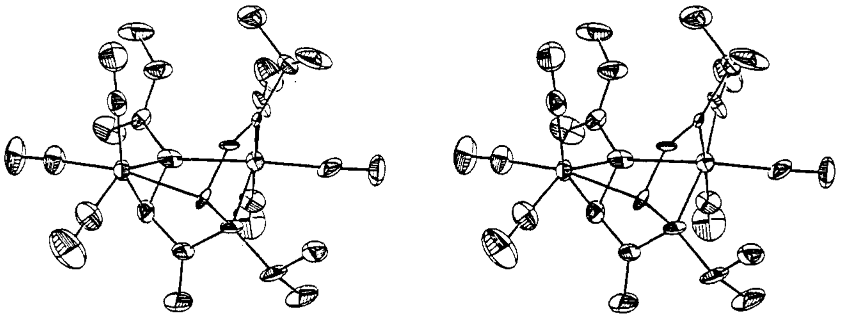


Figure 4. Stereoscopic ORTEP representation of **7a** (ellipsoid probability scale: 30%).

Table III. Fractional Coordinates of the Non-Hydrogen Atoms of 6b and (Equivalent) Isotropic Thermal Parameters (Esd's in Parentheses)

atom	x	y	z	U_{eq}/U, Å^2
Fe(1)	0.2316 (2)	0.3352 (4)	0.5243 (2)	0.047 (2)
Fe(2)	0.3616 (1)	0.3746 (3)	0.5679 (2)	0.038 (2)
C(1)	0.1648 (9)	0.315 (3)	0.571 (1)	0.06 (2)
C(2)	0.182 (1)	0.276 (3)	0.409 (2)	0.07 (2)
C(3)	0.4455 (9)	0.323 (2)	0.595 (1)	0.04 (1)
C(4)	0.3653 (10)	0.452 (2)	0.459 (2)	0.06 (2)
C(5)	0.229 (1)	0.523 (3)	0.487 (2)	0.08 (2)
C(6)	0.3074 (9)	0.150 (3)	0.668 (1)	0.06 (1)
C(7)	0.2811 (7)	0.133 (2)	0.566 (1)	0.03 (1)
C(8)	0.3090 (9)	0.213 (2)	0.505 (1)	0.04 (1)
C(9)	0.3059 (9)	0.144 (2)	0.412 (1)	0.04 (1)
C(10)	0.276 (1)	−0.066 (3)	0.315 (2)	0.10 (2)
C(11)	0.2859 (8)	0.401 (2)	0.666 (1)	0.03 (1)
C(12)	0.3177 (9)	0.556 (2)	0.672 (1)	0.04 (1)
C(13)	0.3892 (9)	0.311 (3)	0.789 (1)	0.05 (1)
C(14)	0.3542 (9)	0.321 (3)	0.867 (1)	0.07 (2)
C(15)	0.4080 (10)	0.353 (3)	0.961 (1)	0.07 (2)
C(16)	0.462 (1)	0.230 (3)	0.983 (2)	0.08 (2)
C(17)	0.4958 (9)	0.220 (3)	0.909 (1)	0.06 (2)
C(18)	0.4443 (9)	0.191 (2)	0.810 (1)	0.04 (1)
C(19)	0.4050 (10)	0.709 (2)	0.660 (1)	0.05 (2)
C(20)	0.4774 (9)	0.673 (2)	0.717 (1)	0.06 (1)
C(21)	0.518 (1)	0.816 (3)	0.740 (2)	0.08 (2)
C(22)	0.5155 (10)	0.890 (3)	0.646 (2)	0.07 (2)
C(23)	0.446 (1)	0.924 (3)	0.586 (1)	0.07 (2)
C(24)	0.403 (1)	0.781 (3)	0.563 (1)	0.06 (2)
N(1)	0.3411 (7)	0.295 (1)	0.6906 (9)	0.027 (9)
N(2)	0.3649 (7)	0.566 (2)	0.638 (1)	0.04 (1)
O(1)	0.1241 (7)	0.294 (2)	0.6074 (10)	0.08 (1)
O(2)	0.1500 (8)	0.237 (2)	0.336 (1)	0.10 (1)
O(3)	0.4970 (7)	0.286 (2)	0.597 (1)	0.08 (1)
O(4)	0.3666 (9)	0.510 (2)	0.390 (1)	0.09 (1)
O(5)	0.2194 (8)	0.643 (2)	0.456 (1)	0.11 (1)
O(6)	0.3079 (6)	0.059 (2)	0.7302 (9)	0.061 (10)
O(7)	0.2825 (8)	0.008 (2)	0.4040 (9)	0.08 (1)
O(8)	0.3237 (8)	0.205 (2)	0.3512 (10)	0.08 (1)

upon heating to 60 °C in a heptane solution through which a stream of nitrogen is passed to give **6** again. These results are shown in Scheme I. The X-ray crystal structures of **6b** and **7a** have been determined.

Molecular Structures of 6b and 7a. The molecular structures of **6b** and **7a** are shown as PLUTO representations in Figures 1 and 2, respectively. The atomic numbering of the ligand backbone is identical for both compounds. Figures 3 and 4 show stereoscopic ORTEP representations of **6b** and **7a**, respectively. Positional parameters and selected bond lengths and angles of **6b** and **7a** are listed in Tables III–VIII. The molecular geometries of **6b** and **7a** show a strong similarity. In both complexes the iron centers are bridged by an 8e-donating organic ligand. The backbone of this ligand is composed of the N–C–C–N skeleton of the R-DAB ligand, the C atom of a CO molecule, and the two alkyne C atoms of a methyl propynoate molecule. The C atom of the CO molecule is linked to both the N(1) atom of the R-DAB ligand and the unsubstituted C(7) atom of the methyl propynoate molecule. In both complexes this new organic ligand is bonded to the metal carbonyl core in a similar fashion. The uncoupled imine moiety of the R-DAB has fully retained its imine character, as is confirmed by the C(12)–N(2) distance of 1.238 (18) Å in **6b** and 1.267 (13) Å in **7a** and is σ-N-coordinated to Fe(2) with the normal Fe–N distances of 1.992 (11) Å in **6b** and 1.997 (8) Å in **7a**. The N(1) atom of the second imine moiety has become linked to the CO molecule via a C–N bond and is also σ-N-coordinated to Fe(2) [N(1)–Fe(2) 2.099 (9) Å in **6b** and 2.060 (9) Å in **7a**]. The former imine C(11) atom is σ-bonded to Fe(1) with almost identical bond lengths in **6b** and **7a** [2.136 (12) and 2.152 (10) Å, respectively]. The reduced alkyne bond C(7)–C(8) is η^2-coordinated to Fe(1) with normal Fe–C bond lengths

Table IV. Selected Bond Lengths (Å) of the Non-Hydrogen Atoms of 6b (Esd's in Parentheses)

Fe(1)–Fe(2)	2.632 (4)	C(4)–O(4)	1.147 (19)
Fe(1)–C(1)	1.744 (14)	C(5)–O(5)	1.16 (2)
Fe(1)–C(2)	1.783 (15)	C(6)–C(7)	1.442 (17)
Fe(1)–C(5)	1.77 (2)	C(6)–N(1)	1.47 (2)
Fe(1)–C(7)	2.088 (12)	C(6)–O(6)	1.223 (18)
Fe(1)–C(8)	2.048 (14)	C(7)–C(8)	1.405 (18)
Fe(1)–C(11)	2.136 (12)	C(8)–C(9)	1.484 (18)
Fe(2)–C(3)	1.747 (14)	C(9)–O(7)	1.307 (17)
Fe(2)–C(4)	1.767 (16)	C(9)–O(8)	1.198 (17)
Fe(2)–C(8)	1.887 (14)	C(10)–O(7)	1.44 (2)
Fe(2)–N(1)	2.099 (9)	C(11)–C(12)	1.533 (19)
Fe(2)–N(2)	1.992 (11)	C(11)–N(1)	1.458 (16)
C(1)–O(1)	1.150 (17)	C(12)–N(2)	1.238 (18)
C(2)–O(2)	1.137 (19)	C(13)–N(1)	1.502 (16)
C(3)–O(3)	1.112 (18)	C(19)–N(2)	1.514 (18)

Table V. Selected Bond Angles (deg) of the Non-Hydrogen Atoms of 6b (Esd's in Parentheses)

Fe(2)-Fe(1)-C(1)	144.5 (5)	Fe(1)-C(1)-O(1)	174.3 (11)
Fe(2)-Fe(1)-C(2)	122.6 (7)	Fe(1)-C(2)-O(2)	179.2 (11)
Fe(2)-Fe(1)-C(5)	83.2 (8)	Fe(2)-C(3)-O(3)	168.8 (11)
Fe(2)-Fe(1)-C(7)	69.9 (4)	Fe(2)-C(4)-O(4)	176.0 (11)
Fe(2)-Fe(1)-C(8)	45.5 (5)	Fe(1)-C(5)-O(5)	171.7 (14)
Fe(2)-Fe(1)-C(11)	60.9 (4)	C(7)-C(6)-N(1)	109.7 (14)
C(1)-Fe(1)-C(2)	91.9 (11)	C(7)-C(6)-O(6)	128.4 (13)
C(1)-Fe(1)-C(5)	105.5 (11)	N(1)-C(6)-O(6)	121.7 (15)
C(1)-Fe(1)-C(7)	100.5 (9)	Fe(1)-C(7)-C(6)	102.4 (12)
C(1)-Fe(1)-C(8)	139.7 (8)	Fe(1)-C(7)-C(8)	68.6 (11)
C(1)-Fe(1)-C(11)	84.4 (9)	C(6)-C(7)-C(8)	120.4 (14)
C(2)-Fe(1)-C(5)	91.9 (11)	Fe(1)-C(8)-Fe(2)	83.9 (9)
C(2)-Fe(1)-C(7)	96.8 (9)	Fe(1)-C(8)-C(7)	71.7 (12)
C(2)-Fe(1)-C(8)	88.3 (9)	Fe(1)-C(8)-C(9)	122.2 (10)
C(2)-Fe(1)-C(11)	176.2 (7)	Fe(2)-C(8)-C(7)	111.9 (12)
C(5)-Fe(1)-C(7)	152.3 (9)	Fe(2)-C(8)-C(9)	129.0 (10)
C(5)-Fe(1)-C(8)	114.8 (10)	C(7)-C(8)-C(9)	117.6 (14)
C(5)-Fe(1)-C(11)	89.8 (10)	C(8)-C(9)-O(7)	112.6 (14)
C(7)-Fe(1)-C(8)	39.7 (6)	C(8)-C(9)-O(8)	124.0 (14)
C(7)-Fe(1)-C(11)	83.1 (7)	O(7)-C(9)-O(8)	123.5 (14)
C(8)-Fe(1)-C(11)	93.9 (7)	Fe(1)-C(11)-C(12)	113.7 (10)
Fe(1)-Fe(2)-C(3)	156.9 (5)	Fe(1)-C(11)-N(1)	102.4 (9)
Fe(1)-Fe(2)-C(4)	98.9 (7)	C(12)-C(11)-N(1)	106.1 (14)
Fe(1)-Fe(2)-C(8)	50.7 (5)	C(11)-C(12)-N(2)	115.4 (14)
Fe(1)-Fe(2)-N(1)	72.5 (4)	Fe(2)-N(1)-C(6)	108.4 (9)
Fe(1)-Fe(2)-N(2)	96.6 (5)	Fe(2)-N(1)-C(11)	85.2 (9)
C(3)-Fe(2)-C(4)	89.8 (10)	Fe(2)-N(1)-C(13)	122.9 (9)
C(3)-Fe(2)-C(8)	108.1 (9)	C(6)-N(1)-C(11)	103.2 (15)
C(3)-Fe(2)-N(1)	99.5 (8)	C(6)-N(1)-C(13)	116.2 (12)
C(3)-Fe(2)-N(2)	103.5 (8)	C(11)-N(1)-C(13)	115.6 (12)
C(4)-Fe(2)-C(8)	92.0 (10)	Fe(2)-N(2)-C(12)	103.8 (12)
C(4)-Fe(2)-N(1)	170.7 (7)	Fe(2)-N(2)-C(19)	140.4 (8)
C(4)-Fe(2)-N(2)	97.2 (9)	C(12)-N(2)-C(19)	115.8 (15)
C(8)-Fe(2)-N(1)	85.4 (7)	C(9)-O(7)-C(10)	116.4 (15)
C(8)-Fe(2)-N(2)	147.1 (6)		
N(1)-Fe(2)-N(2)	80.4 (6)		

Table VI. Fractional Coordinates of the Non-Hydrogen Atoms of 7a and Equivalent Isotropic Thermal Parameters (Esd's in Parentheses)

atom	x	y	z	U_{eq}, Å^2
Fe(1)	0.5551 (2)	0.2807 (1)	0.4795 (2)	0.038 (1)
Fe(2)	0.4857 (2)	0.1202 (1)	0.6991 (2)	0.036 (1)
C(1)	0.619 (1)	0.375 (1)	0.494 (2)	0.07 (1)
C(2)	0.487 (1)	0.328 (1)	0.345 (2)	0.06 (1)
C(3)	0.516 (2)	0.056 (1)	0.841 (2)	0.06 (1)
C(4)	0.368 (1)	0.146 (1)	0.767 (2)	0.06 (1)
C(5)	0.627 (1)	0.224 (1)	0.367 (2)	0.05 (1)
C(6)	0.474 (1)	0.2969 (10)	0.715 (2)	0.048 (10)
C(7)	0.436 (1)	0.283 (1)	0.589 (2)	0.050 (10)
C(8)	0.453 (1)	0.1993 (10)	0.546 (2)	0.048 (10)
C(9)	0.432 (1)	0.0322 (9)	0.621 (2)	0.05 (1)
C(10)	0.393 (1)	0.172 (1)	0.429 (2)	0.043 (10)
C(11)	0.623 (1)	0.2439 (10)	0.658 (1)	0.030 (8)
C(12)	0.661 (1)	0.1668 (9)	0.618 (1)	0.032 (8)
C(13)	0.584 (1)	0.249 (1)	0.894 (2)	0.06 (1)
C(14)	0.507 (2)	0.231 (2)	0.991 (2)	0.11 (2)
C(15)	0.672 (1)	0.202 (1)	0.918 (2)	0.06 (1)
C(16)	0.651 (1)	0.0140 (9)	0.595 (2)	0.045 (10)
C(17)	0.759 (2)	0.011 (1)	0.623 (3)	0.10 (2)
C(18)	0.635 (2)	−0.008 (2)	0.458 (2)	0.09 (2)
C(19)	0.379 (2)	0.067 (1)	0.269 (3)	0.11 (2)
N(1)	0.5447 (10)	0.2319 (7)	0.754 (1)	0.045 (8)
N(2)	0.6146 (8)	0.0997 (7)	0.627 (1)	0.023 (6)
O(1)	0.661 (1)	0.4356 (9)	0.508 (2)	0.12 (1)
O(2)	0.445 (1)	0.358 (1)	0.266 (2)	0.10 (1)
O(3)	0.537 (1)	0.0138 (8)	0.926 (1)	0.076 (9)
O(4)	0.2967 (10)	0.159 (1)	0.801 (2)	0.11 (1)
O(5)	0.668 (1)	0.185 (1)	0.289 (2)	0.10 (1)
O(6)	0.461 (1)	0.3565 (8)	0.787 (1)	0.079 (9)
O(7)	0.4279 (10)	0.1011 (8)	0.377 (1)	0.070 (9)
O(8)	0.3274 (9)	0.2070 (10)	0.388 (2)	0.09 (1)
O(9)	0.392 (1)	−0.0225 (9)	0.587 (2)	0.10 (1)

Table VII. Bond Lengths (Å) of the Non-Hydrogen Atoms of 7a (Esd's in Parentheses)

Fe(1)-C(1)	1.773 (13)	C(6)-N(1)	1.502 (15)
Fe(1)-C(2)	1.848 (14)	C(6)-O(6)	1.225 (15)
Fe(1)-C(5)	1.789 (13)	C(7)-C(8)	1.438 (17)
Fe(1)-C(7)	2.027 (13)	C(8)-C(10)	1.535 (17)
Fe(1)-C(8)	2.067 (11)	C(9)-O(9)	1.103 (16)
Fe(1)-C(11)	2.152 (10)	C(10)-O(7)	1.352 (16)
Fe(2)-C(3)	1.837 (12)	C(10)-O(8)	1.165 (15)
Fe(2)-C(4)	1.853 (14)	C(11)-C(12)	1.413 (15)
Fe(2)-C(8)	2.075 (12)	C(11)-N(1)	1.496 (14)
Fe(2)-C(9)	1.796 (12)	C(12)-N(2)	1.267 (13)
Fe(2)-N(1)	2.061 (9)	C(13)-C(14)	1.50 (2)
Fe(2)-N(2)	1.997 (8)	C(13)-C(15)	1.48 (2)
C(1)-O(1)	1.151 (17)	C(13)-N(1)	1.565 (15)
C(2)-O(2)	1.115 (18)	C(16)-C(17)	1.56 (2)
C(3)-O(3)	1.145 (16)	C(16)-C(18)	1.47 (2)
C(4)-O(4)	1.088 (18)	C(16)-N(2)	1.509 (13)
C(5)-O(5)	1.171 (18)	C(19)-O(7)	1.42 (2)
C(6)-C(7)	1.419 (17)		

Table VIII. Selected Bond Angles (deg) of the Non-Hydrogen Atoms of 7a (Esd's in Parentheses)

C(1)-Fe(1)-C(2)	88.6 (10)	Fe(1)-C(1)-O(1)	177.6 (10)
C(1)-Fe(1)-C(5)	101.6 (9)	Fe(1)-C(2)-O(2)	178.2 (11)
C(1)-Fe(1)-C(7)	111.2 (8)	Fe(2)-C(3)-O(3)	177.1 (9)
C(1)-Fe(1)-C(8)	150.7 (6)	Fe(2)-C(4)-O(4)	176.0 (11)
C(1)-Fe(1)-C(11)	86.3 (9)	Fe(1)-C(5)-O(5)	175.0 (10)
C(2)-Fe(1)-C(5)	91.4 (9)	C(7)-C(6)-N(1)	112.7 (12)
C(2)-Fe(1)-C(7)	88.4 (9)	C(7)-C(6)-O(6)	128.1 (12)
C(2)-Fe(1)-C(8)	98.2 (8)	N(1)-C(6)-O(6)	119.0 (12)
C(2)-Fe(1)-C(11)	169.2 (6)	Fe(1)-C(7)-C(6)	101.1 (11)
C(5)-Fe(1)-C(7)	147.2 (6)	Fe(1)-C(7)-C(8)	70.9 (10)
C(5)-Fe(1)-C(8)	106.7 (8)	C(6)-C(7)-C(8)	111.4 (13)
C(5)-Fe(1)-C(11)	98.9 (8)	Fe(1)-C(8)-Fe(2)	118.9 (6)
C(7)-Fe(1)-C(8)	41.1 (6)	Fe(1)-C(8)-C(7)	68.0 (10)
C(7)-Fe(1)-C(11)	84.5 (7)	Fe(1)-C(8)-C(10)	108.1 (10)
C(8)-Fe(1)-C(11)	81.8 (7)	Fe(2)-C(8)-C(7)	112.3 (10)
C(3)-Fe(2)-C(4)	92.2 (9)	Fe(2)-C(8)-C(10)	122.7 (9)
C(3)-Fe(2)-C(8)	176.4 (6)	C(7)-C(8)-C(10)	114.6 (13)
C(3)-Fe(2)-C(9)	90.5 (9)	Fe(2)-C(9)-O(9)	170.9 (10)
C(3)-Fe(2)-N(1)	100.3 (7)	C(8)-C(10)-O(7)	110.5 (13)
C(3)-Fe(2)-N(2)	89.3 (8)	C(8)-C(10)-O(8)	125.8 (13)
C(4)-Fe(2)-C(8)	86.9 (8)	O(7)-C(10)-O(8)	123.7 (13)
C(4)-Fe(2)-C(9)	87.9 (9)	Fe(1)-C(11)-C(12)	99.5 (9)
C(4)-Fe(2)-N(1)	93.8 (7)	Fe(1)-C(11)-N(1)	105.4 (8)
C(4)-Fe(2)-N(2)	176.5 (6)	C(12)-C(11)-N(1)	111.1 (11)
C(8)-Fe(2)-C(9)	92.9 (8)	C(11)-C(12)-N(2)	122.0 (12)
C(8)-Fe(2)-N(1)	76.3 (6)	Fe(2)-N(1)-C(6)	105.3 (9)
C(8)-Fe(2)-N(2)	91.4 (6)	Fe(2)-N(1)-C(11)	103.5 (8)
C(9)-Fe(2)-N(1)	168.9 (5)	Fe(2)-N(1)-C(13)	123.3 (8)
C(9)-Fe(2)-N(2)	95.2 (7)	C(6)-N(1)-C(11)	103.2 (12)
N(1)-Fe(2)-N(2)	82.8 (5)	C(6)-N(1)-C(13)	111.0 (11)
		C(11)-N(1)-C(13)	108.6 (12)
		Fe(2)-N(2)-C(12)	111.1 (9)
		Fe(2)-N(2)-C(16)	123.0 (7)
		C(12)-N(2)-C(16)	125.9 (11)
		C(10)-O(7)-C(19)	117.4 (14)

for this bonding mode [Fe(1)-C(7) = 2.088 (12) Å and Fe(1)-C(8) = 2.048 (14) Å for **6b** and Fe(1)-C(7) = 2.027 (13) Å and Fe(1)-C(8) = 2.067 (11) Å for **7a**]. Finally, the substituted alkyne C(8) atom is σ-bonded to Fe(2).

Obviously, the most striking structural difference between both compounds is the absence of an Fe-Fe bond in **7a** [Fe(1)···Fe(2) = 3.561 (4) Å], whereas this bond is present in **6b** as indicated by the Fe(1)-Fe(2) distance of 2.632 (4) Å in **6b** which is in the range of a normal single Fe-Fe bond. Clearly this is due to the coordination of an additional CO to Fe(2) in **7a**. All CO ligands in both **6b** and **7a** are terminally bonded with normal bond lengths and angles. Finally, in **6b** the newly formed organic ligand bridges an $Fe(CO)_2$ and an $Fe(CO)_3$ fragment, whereas in **7a** this ligand bridges two $Fe(CO)_3$ fragments.

It is noteworthy that the new organic ligand contributes 8e to the $Fe_2(CO)_n$ core, when regarding the σ-bonded N atoms and the η^2-coordinated olefin as two-electron donors and the σ-bonded C atoms as one-electron donors. Con-

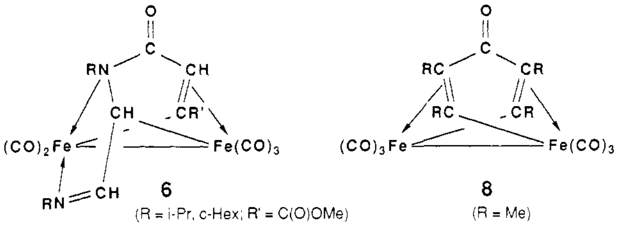
Table IX. ^{1}H NMR Data of $Fe_2(CO)_n\{(R)N{=}C(H)C(H)N(R)C(O)C(H){=}CC(O)OMe\}$ (6a, n = 5, R = i-Pr; 6b, n = 5, R = c-Hex; 7a, n = 6, R = i-Pr; 7b, n = 6, R = c-Hex)^a

	R	N=CH	N—CH	alkyne H	OMe
6a	1.08, 1.23, 1.35, 1.36^b 2.88, 3.70^d	8.12^c	2.89^c	4.31	3.69
6b	1.7 (20 H), 3.3 (2H)^e	8.10^c	2.89^c	4.31	3.70
7a	1.18, 1.24, 1.42, 1.46^b 3.08, 3.79^d	7.89^c	2.71^c	4.24	3.71
7b	1.7 (20 H), 3.2 (2 H)^e	7.83^c	2.67^c	4.25	3.69

[a] Measured in $CDCl_3$; 20 °C, 100 MHz; δ values in ppm relative to internal Me_4Si. [b] Doublets, J = 6 Hz. [c] Doublets, J = 2 Hz. [d] Septets, J = 6 Hz. [e] Multiplets.

sequently the Fe atoms in **7a** do not obey the 18e rule, whereas in **6b** they do. In **7a** Fe(1) possesses formally a 17e configuration while Fe(2) has 19 electrons. The longer Fe(2)-C(8) bond in **7a** [2.075 (12) Å vs 1.887 (14) Å in **6b**] indicates that in **7a** a weaker bonding of C(8) to Fe(2) compensates for this unequal 17/19-electron distribution. The somewhat longer olefinic C(7)-C(8) bond in **7a** [1.438 (17) Å vs 1.405 (18) Å in **6b**] in combination with the slightly shorter Fe(1)-C(7) and Fe(1)-C(8) distances in **7a** [2.027 (13) and 2.067 (11) Å vs 2.088 (12) and 2.048 (14) Å in **6b**] indicates a stronger bonding of Fe(1) to the olefinic C(7)-C(8) fragment in **7a** as compared to this bonding in **6b**. There is no obvious explanation for the unusually short C(11)-C(12) bond length of 1.413 (15) Å in **7a** [cf. the normal value of 1.533 (19) Å for the corresponding single C-C bond in **6b**].

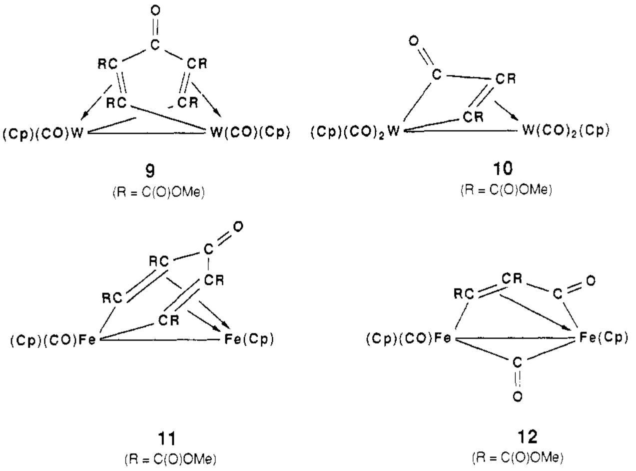
NMR Spectroscopy. The ^{1}H and ^{13}C NMR data are listed in Tables IX and X, respectively. The chemical shifts of the comparable protons in the reported products **6** and **7** have similar values. This indicates that the cleavage of the metal-metal bond and the addition of a CO ligand in the reaction of **6** to **7** do not have a dramatic influence on the geometry of the flyover ligand nor on the bonding within the ligand. In all four reported compounds the former alkyne proton H(7) resonates between 4.24 and 4.31 ppm, while the methoxy protons of the MeOC(O) group appear as sharp singlets between 3.69 and 3.71 ppm. The chemical shifts of the former imine proton on C(11), i.e. 2.89 ppm for **6a** and **6b** and 2.71 and 2.67 ppm for **7a** and **7b** are not very different from the values found for the imine proton on the η^2-coordinated imine group of a σ-N, μ_2-N′, η^2-C=N′ coordinated R-DAB, e.g. in **1**. The proton H(12) on the intact imine group appears as expected between 7.89 and 8.12 ppm.[7] The C(6) atom of the carbonyl molecule bonded to the alkyne as well as the C atoms of the methoxycarbonyl group of the alkyne show the expected chemical shift values. This also applies for the C(12) atom of the σ-N coordinated imine group, which is found between 169 and 175 ppm for **6a**, **6b**, and **7a**.[10] The chemical shifts of the reduced imine C(11) atoms are found at 49.1 ppm for **7a** but at 22.4 and 23.1 ppm for **6b** and **6a**, respectively. The latter two resonances are found at a rather low frequency when compared to the values observed for $Fe_2(CO)_6$(R-DAB), 58.9 and 63.7 ppm for R = i-Pr and c-Hex, respectively, but are consistent with the expected values for an sp^3-hybridized C atom σ-bonded to an Fe atom. The above-mentioned stronger bonding of Fe(1) to C(7)-C(8) in **7a** when compared to **6b** is in agreement with the upfield shift of C(7) in **7a** (δ = 60.1 ppm) with respect to C(7) in **6a** (δ = 64.8 ppm) and **6b** (δ = 68.6 ppm). These chemical shift values are normal for coordinated olefinic carbon atoms. In **6a** the chemical shift of the other olefinic C atom C(8), at 152.9 ppm, agrees with the fact that C(8) is σ-bonded to Fe(2). In **7a** the resonance of C(8) at 88.2 ppm shows a remarkable upfield shift of about 65 ppm with respect to **6**. This shift in **7a** may be explained by our earlier observation that, in order to compensate for the buildup of excess of electron density on Fe(2), the Fe(2)-C(8) bond in **7a** is weakened.



6 (R = i-Pr, c-Hex; R' = C(O)OMe)

8 (R = Me)

Figure 5. Comparison of the ligand geometry and bonding in **6b** and **8**.



9 (R = C(O)OMe)

10 (R = C(O)OMe)

11 (R = C(O)OMe)

12 (R = C(O)OMe)

Figure 6. Compounds **9**–**12**.

Complex Formation. The bridging ligands in the title complexes are, as is shown in Figure 4, isostructural and isoelectronic with the well-known flyover-type ligands formed in many reactions of metal carbonyl clusters with alkynes.[23] In these latter products two alkynes are coupled to a CO molecule to form a –C(R)=C(R)C(O)C(R)=C(R)– fragment bonded to a dinuclear metal carbonyl core via two σ M-C bonds and two η^2-coordinated olefinic fragments. These complexes are assumed to be intermediates in the formation of quinones and other cyclic organic molecules.[23] In complexes **6** and **7**, however, it is the N(1) atom instead of a second olefinic fragment that donates two electrons to Fe(2). Furthermore, the C(11) atom which is σ-bonded to Fe(1) has an imine substituent that is η^2-coordinated to Fe(2). The above-mentioned analogy is confirmed by the bond lengths in the ligands in **6b** and **7a** which are comparable with those in the C=CC(O)C=C flyover-type ligand, e.g. in **8**.[14]

In view of the structural analogy between the presently discussed compounds and those of type **8**, it seems reasonable to assume that the flyover-type ligands in **6** and **8** are formed in mechanistically analogous reactions. Knox et al. reported the ditungsten complex $(Cp)_2W_2(CO)_2$-$(MeOC(O)C{\equiv}CC(O)OMe)_2CO$ (**9**) containing a flyover-type ligand resulting from the coupling of a CO and two dimethyl acetylenedicarboxylate molecules.[24] This compound is assumed to be formed via **10**, upon prolonged irradiation of $(Cp)_2W_2(CO)_6$ in the presence of the alkyne. On the basis of this observation the authors concluded that

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(23) Hübel, W. *Organic Synthesis via Metal Carbonyls*; Wender, I.; Pino, P., Eds.; Interscience; New York, 1968; Vol. I.

(24) Finnimore, S. R., Knox, S. A. R.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* 1982, 1783.

Table X. ^{13}C NMR Data of $Fe_2(CO)_n\{(R)N{=}C(H)C(H)N(R)C(O)C(H){=}CC(O)OMe\}$ (**6a**, $n = 5$, R = *i*-Pr; **6b**, $n = 5$, R = c-Hex; **7a**, $n = 6$, R = *i*-Pr)[a]

	R	N=CH	N–CH	=CH	=CR	C(O)OMe	NC(O)	CO's
6a	18.0, 18.1 21.4, 22.5 53.5, 60.0	174.3	23.1	64.8	152.9	175.3 51.9	181.9	207.1, 208.1 212.7, 213.6 215.9
6b	24.2, 24.6 24.7, 25.4 26.0, 26.2 28.6, 31.3 62.5, 65.0	174.1	22.4	68.6	153	175.5 52.1	181.9	201.4, 203.9 205.8, 213.8 216.0
7a	18.1, 22.2 22.9, 23.1 50.7, 54.4	169.7	49.1	60.1	88.2	179.9 49.9	179.7	201.1, 203.8 205.7, 209.9 211.0, 211.8

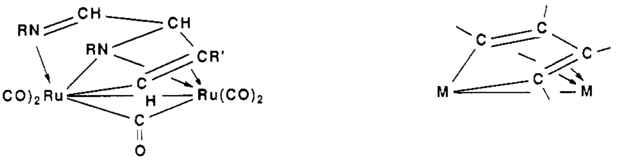
[a] Measured in $CDCl_3$; −20 °C; 62.9 MHz; δ values in ppm relative to internal Me_4Si.

8 was formed via the complex $Fe_2(CO)_6[\sigma,\sigma\text{-}MeC{=}C(Me)C(O)]$, which is isostructural to **10**. Earlier, however, they reported the complex $(Cp)_2Fe_2(CO)(RC{\equiv}CR)_2CO$ (**11**) containing a ferracyclohexadienone fragment, which was assumed to be formed in the reaction of intermediate **12** with a second alkyne molecule.[25]

Complex **6** might be formed via an intermediate of type **10**, with two C atoms σ-bonded to one Fe center and the olefinic fragment π-coordinated to the other Fe center. However, this possibility seems less likely because it would require the insertion of the C(R)=C(H)C(O) fragment, which is σ,σ-bonded to one Fe atom, to insert in the Fe–N bond on the other Fe center. A more reasonable alternative would be the formation of **6** via an intermediate, i.e. **5**, similar to **12**. We propose that **5** is formed in the following fashion (see Scheme I). The first step in the mechanism is the substitution of the η^2-C=N-coordinated imine moiety of the DAB ligand in **1** by the η^2-C≡C coordinated alkyne to give **2**. This proposal is supported by the fact that in the reaction of **1** with dimethyl acetylenedicarboxylate **3** is formed, which reacts in CO atmosphere to give also flyover complexes analogous to **6** and **7**.[26] For the latter reaction a complex analogous to **2** is proposed to be intermediate in the formation of **3**. It seems not unlikely that **3** reacts with CO in the reverse way to give the intermediate **2** again, which then reacts further to give the flyover complexes.

The next step in the formation of **6** and **7** is the intramolecular attack of the coordinated alkyne on one of the CO ligands to give **4**, in which the Fe–Fe bond is bridged by a μ_2-MeOC(O)C=C(H)C(O) unit. Such an intramolecular coupling in an R-DAB complex is not unprecedented since mononuclear $Fe(CO)_2$(R-DAB)(η^2-alkyne) complexes are known to transform into the ferracyclobutenone complexes $Fe(CO)_2$(R-DAB)[RC=C(R)C(O)], containing a similar organic fragment.[27]

Although in this reaction **4** cannot be isolated or observed, a number of structurally analogous and stable complexes are known, such as $Fe_2(CO)_2$(*i*-Pr-Pyca)[μ_2-MeOC(O)C=C(H)C(O)], of which the X-ray crystal structure was solved recently.[28] In the reaction of **1** with methyl propynoate a blue compound, which based on FD-MS, IR, and ^{1}H NMR data is isostructural to this latter complex, can be isolated in very low yields (see Experimental Section).[28] This compound is isomeric with **4** but has the alkyne CH moiety bonded to Fe and the CC(O)OMe (CR′ in Scheme I) moiety bonded to the CO. There is no obvious explanation why this complex does not react further to give a flyover complex, but its isolation is supportive of our view that **4** is a likely intermediate in the formation of **6**.



13
(R = t-Bu, R′ = Ph)

14

Figure 7. Compounds **13** and **14**.

The fact that **6** and the ditungsten compound **9** are apparently formed via different types of intermediates may be the result of the different coordination behavior of alkynes and imine fragments. The proposed mechanism of the recently reported formation of the flyover ligand containing the complex $Fe_2(CO)_6(MeC{\equiv}CNEt_2)_2CO$,[29] resulting from the reaction of $Fe_3(CO)_{12}$ with $MeC{\equiv}CNEt_2$, confirms that flyover ligands can be formed via different types of intermediates.

Finally, **4** is converted to **5** by a substitution of the π-coordinated MeOC(O)C=C(H)C(O) fragment by one η^2-C=N coordinated imine moiety of the chelating R-DAB. Intermediate **5** then reacts further through the N–C bond formation and recoordination of the former alkyne bond via η^2-C=C bonding to give **6**. Direct formation of **7** via the addition of a CO to the $Fe(CO)_2$ fragment in **5** and concomitant N–C coupling can be excluded because, when during the reaction of **1** with methyl propynoate N_2 is bubbled through the solution, **6** is still being formed. While the subsequent formation of **7**, which requires the presence of free CO, is then not observed.[30] If the formation of **6** from **5** were to be induced by initial CO addition, it should also be suppressed under these conditions.

An interesting aspect of these reactions is that the η^2-coordinated imine moiety of the heterodiolefin R-DAB in this case apparently reacts as an alkyne, despite of the differences in chemical and coordination properties of alkynes and imines. Another reaction in which an η^2-coordinated imine group reacted similarly to a coordinated alkyne was reported by us some years ago.[11] The reaction of $Ru_2(CO)_6$(R-DAB) with alkynes R′C≡CR″ yielded the complexes $Ru_2(CO)_5$[AlB(R,R′,R″)][31] (**13**), the structure

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[25] Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 1297.

[26] Part 6 of this series: Muller, F.; Vrieze, K.; van Koten, G.; Duineveld, C. A. A.; Heijdenrijk, D.; Mak, A. J.; Stam, C. H. *Organometallics*, in press.

[27] Frühauf, H.-W., private communication.

[28] Part 5 of this series: Muller, F.; Han, I. M.; Vrieze, K.; van Koten, G.; van Mechelen, J.; Heijdenrijk, D.; Stam, C. H. *Inorg. Chim. Acta*, in press.

[29] Cabrera, E.; Daran, J.-C.; Jeannin, Y.; Kristiansson, O. *J. Organomet. Chem.* **1986**, *310*, 367.

[30] Part 1 of this series: Muller, F.; van Koten, G.; Vrieze, K.; Heijdenrijk, D. *Inorg. Chim. Acta*, in press.

of which may be compared to the metallacyclopentadienyl complexes **14**, which are also very common products in the reactions of metal carbonyls with alkynes. Also in these complexes (**13**) there is a σ-N-coordinated imine group instead of one of the η^2-coordinated olefinic bonds as present in **14**. It is not clear why coupling reactions on Ru complexes involve predominantly C–C coupling whereas on the analogous Fe complexes C–N coupling is favored.[32]

The overall reaction of **1** to **7** may be regarded as an insertion of a μ_2-C(R)=C(H)C(O) fragment into the Fe(1)–N(1) bond, combined with the fission of the metal–metal bond. This conclusion is supported by the small differences between the chemical shifts of the proton on C(11) in **7** and the proton on the η^2-coordinated imine group in **1**. As we noted earlier, however, contrary to **6** complex **7** does not strictly obey the 18e rule, which may account for its facile loss of a CO to give **6**. This reaction, however, appeared to be reversible, which indicates that the formal 17e/19e configuration of **7** does not lead to a significant destabilization with respect to **6**. Finally, we noted that on basis of the structural features of **7**, i.e. a C(8)–Fe(2) distance that is about 0.17 Å longer than in **6**, a weaker σ-bonding of C(8) prevents the buildup of an excess of electron density on Fe(2). This conclusion is in agreement with the results of a theoretical study of diiron complexes with a flyover ligand that shows a predominant σ character in the interaction of the C atoms of the flyover ligand with the metal centers.[33]

Finally, it is well-known that the classical flyover complexes, e.g. the complex $Fe_2(CO)_6$[PhC=C(Ph)C(O)C(Ph)=CPh], can act as a precursor in the formation of quinones, hydroquinones, pyrones, and other organic compounds.[23] We are now currently studying the possibility of utilizing the title compounds as precursors in the formation of new heterocyclic organic molecules.

Conclusions

First, the reactions described in this paper provide a striking example of the chemical activation of an imine group upon η^2-coordination to a metal center. Regarding the structure of the newly formed organic ligands, we can conclude that in these reactions the reactivity of the coordinated imine resembles that of a coordinated alkyne.

Secondly, these results indicate that small differences in the steric and electronic properties of both the R-DAB and the alkyne cause apparently subtle differences in the stability of the intermediates and products, which play an important role in the product distribution of the reactions of $Fe_2(CO)_6$(L) (L = R-DAB, R-Pyca) with alkynes.

Finally, the mildness of the reaction conditions required for the reaction of **6** with CO to give **7** and for the reverse reaction are interesting, indicating a low barrier of activation for metal–metal bond breaking and formation.

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Registry No. **1a**, 74552-74-2; **1b**, 65059-34-9; **6a**, 104407-18-3; **6b**, 104426-23-5; **7a**, 117119-50-3; **7b**, 117120-35-1; Fez(CO)$_6$[(*i*-Pr)NC(H)C(H)N(Pr-*i*)C(H)CC(O)OMe], 104389-73-3; Fez(CO)$_6$[(*c*-Hex)NC(H)C(H)N(*c*-Hex)C(H)CC(O)OMe], 104407-19-4; Fez(CO)$_5$(*i*-Pr-DAB)[μ_2-HC=C(C(O)OMe)C(O)], 117119-49-0; Fez(CO)$_5$(*c*-Hex-DAB)[μ_2-HC=C(C(O)OMe)C(O)], 117120-36-2; methyl propynoate, 922-67-8.

Supplementary Material Available: Tables of anisotropic thermal parameters of the non-hydrogen atoms, the calculated fractional coordinates of the H atoms, bond lengths, and bond angles for **6a** and tables of the anisotropic thermal parameters of the non-hydrogen atoms, the calculated fractional coordinates of the H atoms, and bond angles for **7a** (7 pages); listings of structure factor amplitudes for **6a** and **7a** (16 pages). Ordering information is given on any current masthead page.

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[31] AIB(R,R′,R″) is the abbreviation for the organic ligand resulting from the C–C bond formation between an R-DAB ligand and an alkyne R′C≡CR″. The backbone of the ligand is (R)N=C(H)C(H)N(R)C(R′)=CR″, which is 3-amino-4-imino-1-butene.

[32] There is until now only one example of N–C coupling of an α-diimine N atom to an organic substrate on a Ru complex. This concerns the reaction of $Ru_2(CO)_6$(R-DAB) with ketene ($H_2C=C=O$) to give $Ru_2(CO)_5$[(R)NC(H)C(H)N(R)C(O)CH_2C(O)CH_2] in which a head-to-tail coupled diketene fragment is coupled to the μ_2-N atom of R-DAB.[10]

[33] Casarin, M.; Ajo, D.; Vittadini, A.; Granozzi, G.; Bertoncello, R.; Osella, D. *Inorg. Chem.* **1986**, *25*, 511.