Organometallics 1989, *8*, 41–48

Reversible C–N Bond Formation and Fission between an α-Diimine Ligand and a Methyl Propynoate Molecule on a Dinuclear Iron Carbonyl Moiety. X-ray Crystal Structures of Fe$_2$(CO)$_6${(*i*-Pr)NC(H)C(H)N(*i*-Pr)C(H)CC(O)OMe} and Fe$_2$(CO)$_4${(*i*-Pr)NC(H)C(H)N(*i*-Pr)C(H)CC(O)OMe}[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, Bert B. Krijnen, and Casper H. Stam

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

Received January 14, 1988

Reaction of Fe$_2$(CO)$_6$(*i*-Pr-DAB) (1) with methyl propynoate at 20 °C in hexane solution yields a mixture of products. One of the major products (yield 30%) is the complex Fe$_2$(CO)$_6${(*i*-Pr)NC(H)C(H)N(*i*-Pr)-C(H)CC(O)OMe} (4), of which the molecular structure was elucidated by an X-ray crystal structure determination. Crystals of **4**, $\mathrm{Fe_2C_{18}H_{20}N_2O_8}$, are monoclinic, space group $P2_1/n$, and have cell constants $a = 12.757$ (1) Å, $b = 18.247$ (2) Å, $c = 9.662$ (3) Å, $\beta = 107.35$ (1)°, and $Z = 4$. A total of 3714 absorption-corrected reflections (Mo Kα, $\mu = 14.61$ cm^{-1}) have been used in the refinement resulting in a final R value of 0.051 ($R_w = 0.068$). Complex **4** contains two Fe(CO)$_3$ units which are linked via a single metal–metal bond [Fe–Fe = 2.564 (2) Å] and are bridged by a new 6e-donating ligand, consisting of a μ_2-methylene bridge and a five-membered heterocycle. This heterocycle is formed by coupling of the R-DAB N–C–C–N skeleton via both N atoms to the unsubstituted alkyne C atom of the methyl propynoate. The new ligand is bonded to the metal carbonyl core via a σ-N donor bond, one of the central C atoms of the heterocycle, and the μ_2-methylene C atom. When complex **4** is heated, one of the C–N bonds is broken and the complex Fe$_2$(CO)$_4${(*i*-Pr)NC(H)C(H)N(*i*-Pr)C(H)CC(O)OMe} (5) is formed with concomitant loss of two CO's. Crystals of **5**, $\mathrm{Fe_2C_{16}H_{20}N_2O_6}$, are orthorhombic, space group *Pnca*, and have cell constants $a = 15.209$ (3) Å, $b = 17.685$ (3) Å, $c = 14.489$ (3) Å, and $Z = 8$. A total of 1320 absorption-corrected reflections (Mo Kα, $\mu = 7.60$ cm^{-1}) have been used in the refinement resulting in a final R value of 0.088 ($R_w = 0.107$). Complex **5** consists of two Fe(CO)$_2$ units which are linked by a single metal–metal bond [Fe–Fe = 2.496 (3) Å] and are bridged by a formally 10e-donating ligand via a μ_2-bridging N atom, an azaallyl function, a σ-coordinated N atom, and a π-bonded olefinic fragment, of which the terminal C atom is also σ-bonded to one of the Fe centers. The spectroscopic data (IR, field-desorption mass, and ^{1}H and ^{13}C NMR) of **4** and **5** in solution are consistent with the molecular structures found for the compounds in the solid state. An unique observation is the reversibility of the C–N bond fission: thermal conversion of **4** gives **5** while **5** reacts with CO at 20 °C to give **4** again in good yield.

Introduction

In the past decade the reactivity and versatile coordination behavior of the α-diimine ligand R-DAB [= 1,4-diaza-1,3-butadiene; RN═C(H)C(H)═NR] toward metal carbonyl complexes has proven to result in a rich chemistry.[2a–d] Of particular interest are the many reactions in which C–C coupling reactions occur between the C atom of a π-coordinated imine C═N fragment and an unsaturated organic substrate.[3a–c] This ability of the coordinated R-DAB ligand to undergo C–C coupling reactions is ascribed to the activation of the imine group upon η^2-coordination to a metal center. There are significantly fewer examples of reactions involving the coupling of an organic substrate to the N atom of the η^2-coordinated imine group. The first example was reported by us some years ago[4] and concerned the reaction of Ru$_2$(CO)$_6$(R-DAB) (R = *i*-Pr, c-Hex), in which the DAB ligand is bonded in the σ-N, μ_2-N′, η^2-C═N′ 6e-donating bonding mode, with gaseous ketene. This reaction yielded the complex Ru$_2$(CO)$_5$-[(R)NC(H)C(H)N(R)C(O)CH$_2$C(O)CH$_2$] in which a head to tail coupled diketene fragment is C–N coupled to the DAB ligand.

Another, recent, example involves the reaction of Fe$_2$(CO)$_6$(R-DAB) (R = *i*-Pr, c-Hex) with methyl propynoate, which produces the complexes Fe$_2$(CO)$_n${(R)N═C(H)C(H)N(R)C(O)C(H)═CC(O)OMe} (7, n = 5; 8, n = 6). Both complexes contain a flyover-type ligand resulting from the N–C coupling of an imine group of the R-DAB with a C(O)C(H)═CC(O)OMe moiety that was initially formed by the coupling of a CO and a methyl propynoate molecule.[5,6] In the reaction of Fe$_2$(CO)$_6$(R-DAB) with methyl propynoate also some other products are formed. One of these complexes is Fe$_2$(CO)$_6${(R)NC(H)═C(H)N(R)C(H)-CC(O)OMe} (4) which contains a five-membered heterocyclic ligand in which both N atoms of the R-DAB ligand are coupled to the same alkyne C atom. The resulting new

---

* To whom correspondence should be addressed.

(1) Reactions of Dinuclear Metal Carbonyl α-Diimine Complexes with Alkynes. 3. Part 2: see ref 6.

(2) (a) van Koten, G.; Vrieze, K. *Adv. Organomet. Chem.* **1982**, *21*, 151. (b) Vrieze, K. *J. Organomet. Chem.* **1986**, *300*, 307. (c) van Koten, G.; Vrieze, K. *Recl. Trav. Chim. Pays-Bas* **1981**, *100*, 129. (d) van Koten, G.; Vrieze, K. *Inorg. Chim. Acta* **1985**, *100*, 79.

(3) (a) Staal, L. H.; van Koten, G.; Vrieze, K.; van Santen, B.; Stam, C. H. *Inorg. Chem.* **1981**, *20*, 3598. (b) Keijsper, J.; Polm, L. H.; van Koten, G.; Vrieze, K.; Stam, C. H.; Schagen, J. D. *Inorg. Chim. Acta* **1985**, *103*, 137. (c) Staal, L. H.; Polm, L. H.; Balk, R. W.; van Koten, G.; Vrieze, K.; Brouwers, A. M. F. W. *Inorg. Chem.* **1980**, *19*, 3343.

(4) Polm, L. H.; van Koten, G.; Vrieze, K.; Stam, C. H.; van Tunen, W. C. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1177.

(5) Muller, F.; van Koten, G.; Vrieze, K.; Krijnen, L. B.; Stam, C. H. *J. Chem. Soc., Chem. Commun.* **1986**, 150.

(6) Part 2 of this series: Muller, F.; van Koten, G.; Vrieze, K.; Heijdenrijk, D. *Organometallics*, preceding paper in this issue.

0276-7333/89/2308-0041$01.50/0

organic ligand is bridging both Fe centers. Interestingly, this product (4) appeared to react thermally to give $Fe_2(CO)_4\{(R)NC(H)C(H)N(R)C(H)CC(O)OMe\}$ (5), obviously resulting from the cleavage of one of the formed N–C bonds. The formation of these products was reported in a preliminary form. We now report a more detailed study of the formation and molecular structure of the latter two compounds as well as the remarkable transformation of 4 to 5 that involves a reversible C–N bond formation and fission.

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 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 and columns of generally 20–30 cm length and 1–2 cm diameter. $Fe_2(CO)_6$(*i*-Pr-DAB) was prepared according to known procedures.[3c] Methyl propynoate and CO were used as commercially obtained.

Synthesis of $Fe_2(CO)_6\{(R)NC(H)C(H)N(R)C(H)CC(O)OMe\}$ (4). $Fe_2(CO)_6$(*i*-Pr-DAB) (1; 2 mmol, 840 mg) and methyl propynoate (6 mmol, 504 mg) were stirred in 50 mL of hexane at 20 °C for 24 h. The solvent and excess 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). 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 the complexes $Fe_2(CO)_n\{(i\text{-Pr})N{=}C(H)C(H)N(i\text{-Pr})C(O)C(H){=}CC(O)OMe\}$ (7, *n* = 5, 8, *n* = 6).[6] Further elution with hexane/diethyl ether (1:1) and hexane/diethyl ether (1:3) produced the yellow complex $Fe_2(CO)_6\{(R)NC(H)C(H)N(R)C(H)CC(O)OMe\}$ (4) in an average yield of 30% based on 1. The subsequent fraction produced in low yield the blue complex $Fe_2(CO)_5(R\text{-DAB})[\mu_2\text{-}HC{=}C(C(O)OMe)\text{-}C(O)]$ (6).[7] Product 4 was recrystallized from hexane/diethyl ether at −20 °C, yielding dark yellow crystals suitable for X-ray crystallography. IR [ν(CO), hexane solution, cm^{-1}]: 2064 (m), 2022 (s), 1996 (s), 1981 (s), 1957 (m), 1707 (m). FD mass: *M* 504 (calcd 504.06). Elemental Anal. Found (Calcd for $Fe_2C_{18}H_{20}N_2O_8$): C, 42.96 (42.89); H, 4.01 (4.00); N, 5.52 (5.56). ^1H NMR (δ in ppm relative to internal Me_4Si, $CDCl_3$, 293 K, 250 MHz): 1.05 (6 H, doublet, *J* = 6 Hz, *i*-Pr Me); 1.08, 1.20 (3 H, 3 H, doublets, *J* = 6 Hz, *i*-Pr Me); 2.74, 3.06 (1 H, 1 H, sept., *J* = 6 Hz, *i*-Pr CH); 3.75 (d, *J* = 7 Hz, H(9)); 3.84 (s, OMe); 6.58 (br, H(8)); 6.71 (d, *J* = 7 Hz, H(10)). ^{13}C NMR (δ in ppm relative to internal Me_4Si, $CDCl_3$, 293 K, 25 MHz): 19.6, 21.2, 22.3, 22.5 (*i*-Pr Me); 51.8 (OMe); 53.9 (C(8)); 58.1, 65.4 (*i*-Pr CH); 65.2 (C9)); 101.3 (C(10)); 178.6 (C(O)O); 212.0 (CO's); 212.8 (C(13)).

Synthesis of $Fe_2(CO)_4\{(R)NC(H)C(H)N(R)C(H)CC(O)OMe\}$ (5). Method A. A yellow solution of 4 (0.5 mmol, 252 mg) in 50 mL of heptane was refluxed. The color of the solution slowly changed to brown, and a brown solid precipitated, probably due to some decomposition. After about an hour, when in the IR spectrum of the reaction mixture the bands due to 4 were replaced by those of 5, the reaction was stopped and the solvent evaporated. The crude reaction product was purified by column chromatography. A brown solution of 5 was obtained by elution with hexane/diethyl ether (3:2) in about 50% yield, based on 4. Recrystallization at −80 °C yielded brown crystals, suitable for X-ray crystallography. IR (ν(CO), hexane solution, cm^{-1}): 2010 (s), 1976 (s), 1937 (s), 1929 (s), 1696 (w). FD mass: *M* 448 (calcd 448.04). Elemental Anal. Found: Calcd for $Fe_2C_{16}H_{20}N_2O_6$): C, 41.72 (42.89); H, 4.62 (4.50); N, 5.91 (6.25). ^1H NMR (δ in ppm relative to internal Me_4Si, $CDCl_3$, 293 K, 100 MHz): 0.96, 1.17, 1.47, 1.63 (doublets, *J* = 6 Hz, *i*-Pr Me); 2.73, 3.97 (sept, *J* = 6 Hz, *i*-Pr CH); 3.50 (s, H(5)); 3.89 (s, OMe); 6.48 (s, H(13)); 6.70 (s, H(6)). ^{13}C NMR (δ in ppm relative to internal Me_4Si, $CDCl_3$, 273 K, 62.9 MHz): 20.1, 20.5, 27.4, 28.4 (*i*-Pr Me); 52.4 (OMe); 57.0, 63.5 (*i*-Pr CH); 75.2 (C(5)); 113.0 (C(6)); 114.9 (C(13)); 169.4 (C(14)); 174.9 (C(O)O); 209.1, 210.5, 210.9, 216.3 (CO's).

Table I. Crystallographic Data for 4 and 5

	4	5
formula, mol wt	$Fe_2C_{18}H_{20}N_2O_8$, 504.06	$Fe_2C_{16}H_{20}N_2O_6$, 448.04
cryst system	monoclinic	orthorhombic
space group	$P2_1/n$	*Pnca*
a, Å	12.757 (1)	15.209 (3)
b, Å	18.247 (2)	17.685 (3)
c, Å	9.662 (3)	14.489 (3)
α, deg	90	90
β, deg	107.35 (1)	90
γ, deg	90	90
V, $Å^3$	2049	3897.1
d_{calcd}, *Z*	1.63 g·cm^{-1}, 4	1.52 g·cm^{-1}, 8
μ, cm^{-1}	14.61	7.60
cyst color, size	yellow, 0.30 × 0.30 × 0.18 mm^3	brown, 0.40 × 0.40 × 0.23 mm^3
radiatn	Mo Kα, λ = 0.71069 Å	Mo Kα, λ = 0.71069 Å
2θ range, deg	2.2–64	2.2–60
no. of reflectns	7600	6233
no. with $I < 2.5\sigma(I)$	3886	4913
no. of reflctns in refinement	3714	1320
h min, max	−18, 18	0, 20
k min, max	−26, 0	0, 24
l min, max	−14, 0	0, 18
absorptn corr	DIFABS	DIFABS
extinctn corr	isotropic	no
weighting scheme	$w = 1/(4.36 + F_o + 0.024F_o^2)$	$w = 1/(2.96 + F_o + 0.0276F_o^2)$
anomalous scattering	Fe	Fe
final *R*, R_W	0.051, 0.068	0.088, 0.107

Method B. Methyl propynoate (6 mmol, 504 mg) and 1 (2 mmol, 840 mg) were refluxed in 50 mL of heptane for 2 h. The crude reaction mixture was separated by column chromatography. The hexane fraction contained a small amount of $Fe(CO)_3$(*i*-Pr-DAB). Elution with hexane/diethyl ether (4:1) yielded a minor amount of an as yet unidentified yellow product. Further elution produced a faintly purple colored fraction containing a small amount of an unidentified organometallic compound and small amounts of 1,2,4-tris(methoxycarbonyl)benzene and 1,3,5-tris(methoxycarbonyl)benzene. Complex 5 was obtained by elution with hexane/diethyl ether (3:2) in about 15% yield, based on 1. Finally, elution with hexane/diethyl ether (1:4) and pure diethyl ether, respectively, yielded two regioisomeric compounds $Fe_2(CO)_4(i\text{-Pr-DAB})(HC{\equiv}CC(O)OMe)_2$ (10 and 11).[8] The workup procedure of 5 was the same as described for method A.

Reaction of 5 with CO. A solution of 5 (1 mmol, 448 mg) in 30 mL of diethyl ether was stirred for 90 min at 20 °C under 1.5 atm of CO, during which some precipitation occurred, probably due to decomposition. After the reaction, the solvent was evaporated and the crude product purified by column chromatography. A yellow solution of 4 was obtained by elution with hexane/diethyl ether (1:3) in about 75% yield, based on 5.

Crystal Structure Determinations of $Fe_2(CO)_6\{(R)NC(H)C(H)N(R)C(H)CC(O)OMe\}$ (4) and $Fe_2(CO)_4\{(R)NC(H)$-

---

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

(8) These compounds contain two coupled alkynes (head-to-tail and tail-to-tail, respectively) bonded to an $Fe(CO)_3$ unit forming a ferracyclopentadienyl fragment, bonded to a Fe(CO)(σ,σ-N,N′-R-DAB) unit.[9]

(9) Part 4 of this series: Muller, F.; Han, I. M.; van Koten, G.; Vrieze, K.; Heijdenrijk, D.; de Jong, R. L.; Zoutberg, M. C. *Inorg. Chim. Acta*, in press.

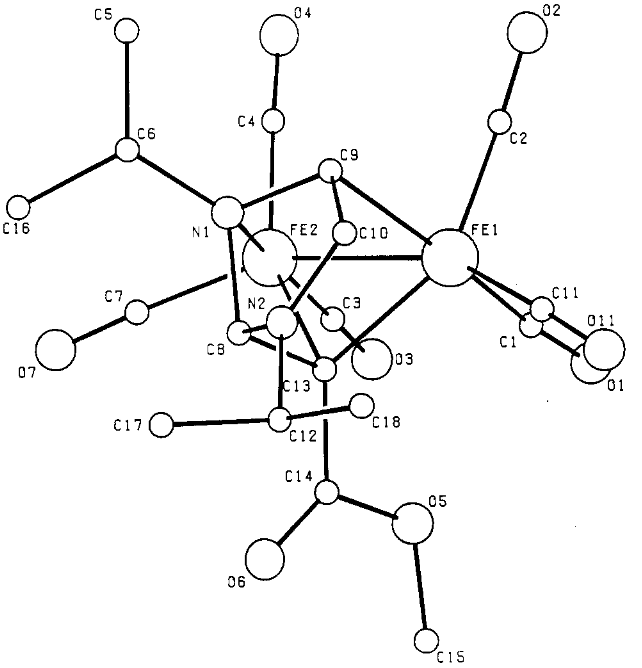


Figure 1. PLUTO drawing of 4. The H atoms are omitted for clarity.

N(R)C(H)CC(O)OMe} (5). The crystal, data aquisition, and refinement parameters are summarized in Table I. The reflections were measured on a Nonius CAD4 diffractometer (θ–2θ scan, 25 °C), and those with $I < 2.5\sigma(I)$ level were treated as unobserved. The structures were solved by means of the heavy-atom method. The positions of the Fe atoms of 4 were located by using the symbolic addition program set SIMPEL,[10] and those of 5 were derived from an E^2 Patterson synthesis. The positions of the H atoms of 4 were calculated and not refined, and those of 5 were excluded. The non-hydrogen atoms of 4 were further refined anisotropically, using block-diagonal least-squares calculations. The C, N, and O atoms of 5 were refined isotropically, while the Fe atoms were refined anisotropically. An empirical absorption correction (DIFABS)[11] was applied. The anomalous dispersion of Fe was taken into account. The calculations were performed with XRAY76;[12] the atomic scattering factors were taken from Cromer and Mann (1968)[13] and the dispersion correction factors from the ref 14.

Results and Discussion

$Fe_2(CO)_6$(*i*-Pr-DAB) (1) reacts thermally with methyl propynoate at 20 °C to give of complex mixture that could fortunately be separated by column chromatography into a number of products. Two of the major products, $Fe_2(CO)_n$\{(*i*-Pr)N=C(H)C(H)N(*i*-Pr)C(O)C(H)=CC(O)OMe\} (7, $n = 5$; 8, $n = 6$), were isolated with a total yield of about 50%.[6] The third major product is $Fe_2(CO)_6$[(*i*-Pr)NC(H)C(H)N(*i*-Pr)C(H)CC(O)OMe] (4) which upon heating to above 90 °C is converted into $Fe_2(CO)_4$\{(*i*-Pr)NC(H)C(H)N(*i*-Pr)C(H)CC(O)OMe\} (5). This latter compound reacts at 20 °C with CO to give 4 again. These products are shown in Scheme I. The molecular structures of 4 and

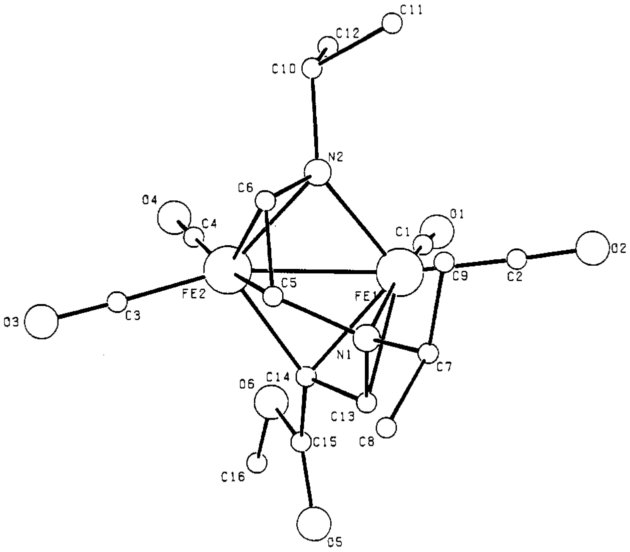


Figure 2. PLUTO drawing of 5.

Table II. Fractional Coordinates and Equivalent Isotropic Thermal Parameters (Å²) of the Non-Hydrogen Atoms of 4

Atom	X	Y	Z	U_{eq}
Fe(1)	0.28123 (6)	0.11198 (4)	0.86541 (8)	0.0327 (3)
Fe(2)	0.20432 (5)	0.11046 (4)	0.58813 (7)	0.0295 (3)
C(1)	0.2341 (5)	0.0225 (3)	0.8922 (6)	0.043 (3)
C(2)	0.4181 (5)	0.0794 (3)	0.8840 (7)	0.046 (3)
C(3)	0.1549 (4)	0.0193 (3)	0.5857 (6)	0.039 (3)
C(4)	0.3228 (5)	0.0796 (3)	0.5370 (7)	0.046 (3)
C(5)	0.3827 (6)	0.2562 (4)	0.5124 (8)	0.059 (4)
C(6)	0.2820 (5)	0.2780 (3)	0.5572 (6)	0.038 (3)
C(7)	0.1035 (5)	0.1296 (3)	0.4166 (6)	0.043 (3)
C(8)	0.1522 (4)	0.2281 (2)	0.6927 (5)	0.027 (2)
C(9)	0.336 (4)	0.2111 (3)	0.7908 (5)	0.032 (2)
C(10)	0.2946 (4)	0.2597 (3)	0.8807 (6)	0.037 (3)
C(11)	0.2799 (6)	0.1364 (4)	1.0438 (7)	0.055 (4)
C(12)	0.1132 (5)	0.3180 (3)	0.8777 (7)	0.044 (3)
C(13)	0.1374 (4)	0.1494 (2)	0.7370 (5)	0.029 (2)
C(14)	0.0248 (4)	0.1324 (3)	0.7393 (5)	0.033 (2)
C(15)	−0.0889 (5)	0.0439 (4)	0.8025 (8)	0.054 (4)
C(16)	0.1865 (6)	0.2988 (4)	0.4233 (7)	0.058 (4)
C(17)	0.0720 (8)	0.3850 (5)	0.7805 (9)	0.077 (5)
C(18)	0.1669 (7)	0.3426 (5)	1.0323 (8)	0.068 (5)
N(1)	0.2519 (3)	0.2170 (2)	0.6438 (4)	0.029 (2)
N(2)	0.1915 (3)	0.2776 (2)	0.8184 (4)	0.032 (2)
O(1)	0.2118 (4)	−0.0354 (3)	0.9199 (6)	0.069 (3)
O(2)	0.5036 (4)	0.0587 (3)	0.887 (7)	0.073 (3)
O(3)	0.1218 (4)	−0.0387 (2)	0.5804 (6)	0.061 (3)
O(4)	0.3954 (5)	0.0568 (3)	0.5066 (8)	0.084 (4)
O(5)	0.0162 (3)	0.0647 (2)	0.7898 (5)	0.047 (2)
O(6)	−0.0524 (3)	0.1738 (2)	0.7020 (5)	0.045 (2)
O(7)	0.0368 (5)	0.1370 (3)	0.3088 (6)	0.076 (3)
O(11)	0.2736 (7)	0.1482 (4)	1.1583 (3)	0.099 (5)

Table III. Bond Distances (Å) of the Non-Hydrogen Atoms of 4 (Esd's in Parantheses)

Fe(1)–Fe(2)	2.564 (2)	C(6)–N(1)	1.509 (5)
Fe(1)–C(1)	1.785 (4)	C(7)–O(7)	1.140 (6)
Fe(1)–C(2)	1.802 (5)	C(8)–C(13)	1.526 (5)
Fe(1)–C(9)	2.127 (4)	C(8)–N(1)	1.497 (5)
Fe(1)–C(11)	1.785 (5)	C(8)–N(2)	1.476 (5)
Fe(1)–C(13)	2.004 (4)	C(9)–C(10)	1.430 (5)
Fe(2)–C(3)	1.777 (4)	C(9)–N(1)	1.494 (5)
Fe(2)–C(4)	1.814 (5)	C(10)–N(2)	1.314 (5)
Fe(2)–C(7)	1.803 (4)	C(11)–O(11)	1.153 (7)
Fe(2)–C(13)	2.009 (4)	C(12)–C(17)	1.536 (8)
Fe(2)–N(1)	2.060 (3)	C(12)–C(18)	1.514 (7)
C(1)–O(1)	1.146 (5)	C(12)–N(2)	1.487 (6)
C(2)–O(2)	1.142 (6)	C(13)–C(14)	1.476 (5)
C(3)–O(3)	1.135 (5)	C(14)–O(5)	1.345 (5)
C(4)–O(4)	1.131 (7)	C(14)–O(6)	1.208 (5)
C(5)–C(6)	1.526 (7)	C(15)–O(5)	1.433 (6)
C(6)–C(16)	1.537 (6)		

---

(10) Overbeek, A. R.; Schenk, H. *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, 1978.

(11) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158.

(12) Stewart, J. M. The XRAY76 system, Technical Report TR446; Computer Science Center, University of Maryland, College Park, MD, 1976.

(13) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. B:* **1968**, *A24*, 321.

(14) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, 1974; Vol. IV.

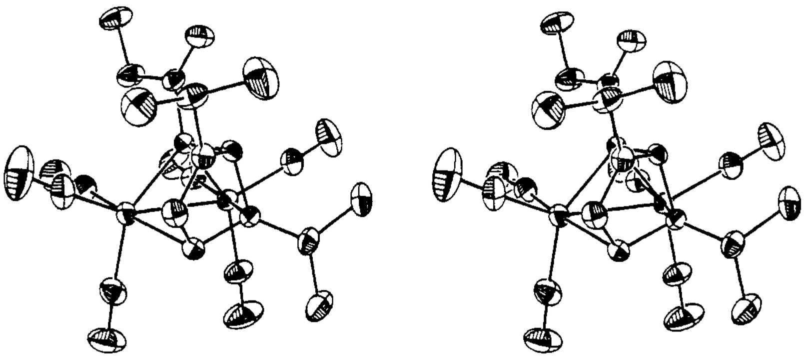


Figure 3. Stereoscopic ORTEP representation of 4 (ellipsoid probability scale 30%).

Table IV. Selected Bond Angles (deg) of the Non-Hydrogen Atoms of 4 (Esd's in Parentheses)

Fe(2)–Fe(1)–C(9)	73.51 (15)	Fe(1)–C(13)–C(8)	109.1 (3)
Fe(2)–Fe(1)–C(13)	50.37 (14)	Fe(1)–C(13)–C(14)	129.4 (3)
C(9)–Fe(1)–C(13)	79.8 (2)	Fe(2)–C(13)–C(8)	91.0 (3)
Fe(1)–Fe(2)–C(13)	50.20 (14)	Fe(2)–C(13)–C(14)	124.0 (3)
Fe(1)–Fe(2)–N(1)	74.08 (12)	C(8)–C(13)–C(14)	113.8 (4)
C(13)–Fe(2)–N(1)	68.54 (18)	Fe(2)–N(1)–C(6)	130.9 (2)
C(13)–C(8)–N(1)	98.6 (4)	Fe(2)–N(1)–C(8)	89.9 (3)
C(13)–C(8)–N(2)	112.6 (3)	Fe(2)–N(1)–C(9)	104.4 (3)
N(1)–C(8)–N(2)	103.3 (4)	C(6)–N(1)–C(8)	117.1 (3)
Fe(1)–C(9)–C(10)	96.9 (3)	C(6)–N(1)–C(9)	111.1 (4)
Fe(1)–C(9)–N(1)	100.5 (3)	C(8)–N(1)–C(9)	97.3 (4)
C(10)–C(9)–N(1)	105.2 (4)	C(8)–N(2)–C(10)	105.8 (4)
C(9)–C(10)–N(2)	111.0 (4)	C(8)–N(2)–C(12)	121.2 (4)
Fe(1)–C(13)–Fe(2)	79.4 (2)	C(10)–N(2)–C(12)	130.0 (4)

Table V. Fractional Coordinates and (Equivalent) Isotropic Thermal Parameters (Å^2) of the Non-Hydrogen Atoms of 5

atom	x	y	z	U_{eq}/U
Fe(1)	0.1754 (2)	0.2834 (1)	0.3375 (2)	0.043 (1)
Fe(2)	0.0897 (2)	0.2217 (1)	0.2114 (2)	0.045 (1)
C(1)	0.260 (1)	0.219 (1)	0.354 (1)	0.061 (5)
C(2)	0.229 (1)	0.349 (1)	0.408 (1)	0.059 (5)
C(3)	0.003 (1)	0.188 (1)	0.150 (2)	0.067 (5)
C(4)	0.148 (1)	0.139 (1)	0.183 (1)	0.051 (5)
C(5)	0.031 (1)	0.3235 (10)	0.240 (1)	0.048 (4)
C(6)	0.098(1)	0.3317 (10)	0.171 (1)	0.052 (4)
C(7)	0.041 (1)	0.413 (1)	0.379 (1)	0.056 (4)
C(8)	−0.060 (1)	0.426 (1)	0.389 (2)	0.071 (6)
C(9)	0.082 (1)	0.477 (1)	0.320 (1)	0.068 (5)
C(10)	0.250 (2)	0.317 (1)	0.130 (1)	0.071 (5)
C(11)	0.290 (2)	0.398 (2)	0.148 (2)	0.158 (9)
C(12)	0.320 (2)	0.261 (2)	0.144 (2)	0.113 (8)
C(13)	0.054 (1)	0.2701 (9)	0.395 (1)	0.036 (3)
C(14)	0.073 (1)	0.2070 (8)	0.344 (1)	0.035 (3)
C(15)	0.068 (1)	0.135 (1)	0.398 (1)	0.049 (4)
C(16)	0.110 (2)	0.004 (1)	0.409 (2)	0.106 (7)
N(1)	0.0595 (9)	0.3362 (7)	0.338 (1)	0.047 (4)
N(2)	0.1779 (9)	0.3050 (7)	0.2021 (10)	0.048 (4)
O(1)	0.314 (1)	0.1729 (8)	0.369 (1)	0.083 (5)
O(2)	0.265 (1)	0.3933 (9)	0.453 (1)	0.096 (5)
O(3)	−0.057 (1)	0.1685 (9)	0.105 (1)	0.104 (4)
O(4)	0.188 (1)	0.0839 (10)	0.168 (1)	0.116 (4)
O(5)	0.018 (1)	0.1251 (8)	0.462 (1)	0.085 (3)
O(6)	0.116 (1)	0.0797 (8)	0.364 (1)	0.095 (3)

Table VI. Bond Distances (Å) of the Non-Hydrogen Atoms of 5 (Esd's in Parentheses)

Fe(1)–Fe(2)	2.496 (3)	C(4)–O(4)	1.169 (19)
Fe(1)–C(1)	1.735 (15)	C(5)–C(6)	1.435 (18)
Fe(1)–C(2)	1.748 (15)	C(5)–N(1)	1.502 (17)
Fe(1)–C(13)	2.039 (11)	C(6)–N(2)	1.379 (16)
Fe(1)–C(14)	2.064 (11)	C(7)–C(8)	1.56 (2)
Fe(1)–N(1)	1.995 (10)	C(7)–C(9)	1.55 (2)
Fe(1)–N(2)	1.999 (10)	C(7)–N(1)	1.509 (17)
Fe(2)–C(3)	1.699 (15)	C(10)–C(11)	1.58 (3)
Fe(2)–C(4)	1.759 (14)	C(10)–C(12)	1.47 (2)
Fe(2)–C(5)	2.052 (12)	C(10)–N(2)	1.529 (18)
Fe(2)–C(6)	2.035 (13)	C(13)–C(14)	1.369 (16)
Fe(2)–C(14)	1.955 (12)	C(13)–N(1)	1.434 (15)
Fe(2)–N(2)	1.997 (10)	C(14)–C(15)	1.496 (17)
C(1)–O(1)	1.177 (19)	C(15)–O(5)	1.212 (17)
C(2)–O(2)	1.157 (18)	C(15)–O(6)	1.316 (17)
C(3)–O(3)	1.17 (2)	C(16)–O(6)	1.49 (2)

Table VII. Selected Bond Angles (deg) of the Non-Hydrogen Atoms of 5 (Esd's in Parentheses)

Fe(2)–Fe(1)–C(13)	77.0 (5)	Fe(2)–C(6)–N(2)	68.5 (10)
Fe(2)–Fe(1)–C(14)	49.7 (4)	C(5)–C(6)–N(2)	111.3 (15)
Fe(2)–Fe(1)–N(1)	75.3 (4)	Fe(1)–C(13)–C(14)	71.5 (10)
Fe(2)–Fe(1)–N(2)	51.3 (3)	Fe(1)–C(13)–N(1)	67.5 (9)
C(13)–Fe(1)–C(14)	39.0 (5)	C(14)–C(13)–N(1)	110.0 (14)
C(13)–Fe(1)–N(1)	41.6 (5)	Fe(1)–C(14)–Fe(2)	76.7 (6)
C(13)–Fe(1)–N(2)	116.1 (6)	Fe(1)–C(14)–C(13)	69.5 (10)
C(14)–Fe(1)–N(1)	68.9 (6)	Fe(1)–C(14)–C(15)	128.3 (9)
C(14)–Fe(1)–N(2)	100.6 (6)	Fe(2)–C(14)–C(13)	116.7 (10)
N(1)–Fe(1)–N(2)	86.0 (6)	Fe(2)–C(14)–C(15)	129.3 (9)
Fe(1)–Fe(2)–C(5)	72.3 (5)	C(13)–C(14)–C(15)	113.6 (14)
Fe(1)–Fe(2)–C(6)	76.1 (5)	Fe(1)–N(1)–C(5)	100.5 (9)
Fe(1)–Fe(2)–C(14)	53.6 (4)	Fe(1)–N(1)–C(7)	126.0 (8)
Fe(1)–Fe(2)–N(2)	51.4 (3)	Fe(1)–N(1)–C(13)	70.9 (9)
C(5)–Fe(2)–C(6)	41.1 (6)	C(5)–N(1)–C(7)	116.9 (12)
C(5)–Fe(2)–C(14)	82.1 (7)	C(5)–N(1)–C(13)	113.9 (12)
C(5)–Fe(2)–N(2)	70.0 (7)	C(7)–N(1)–C(13)	119.8 (13)
C(6)–Fe(2)–C(14)	114.7 (7)	Fe(1)–N(2)–Fe(2)	77.3 (6)
C(6)–Fe(2)–N(2)	40.0 (6)	Fe(1)–N(2)–C(6)	111.7 (10)
C(14)–Fe(2)–N(2)	104.6 (6)	Fe(1)–N(2)–C(10)	135.3 (8)
Fe(2)–C(5)–C(6)	68.8 (11)	Fe(2)–N(2)–C(6)	71.5 (10)
Fe(2)–C(5)–N(1)	101.3 (10)	Fe(2)–N(2)–C(10)	129.1 (9)
C(6)–C(5)–N(1)	116.0 (14)	C(6)–N(2)–C(10)	111.2 (14)
Fe(2)–C(6)–C(5)	70.1 (11)		

5 were confirmed by X-ray crystal structure analyses.

Molecular Structures of 4 and 5. Figures 1 and 2 show PLUTO drawings of 4 and 5, respectively, with the adopted atomic numbering. Figures 3 and 4 show stereoscopic ORTEP representations of 4 and 5. Positional parameters, bond lengths, and selected bond angles of 4 and 5 are listed in Tables II–VII.

In 4 two $Fe(CO)_3$ units, with all CO's terminally bonded with normal bond distances and angles, are linked via a single Fe–Fe bond [Fe(1)–Fe(2) = 2.564 (2) Å] and are bridged by a formally 6e-donating organic ligand. This ligand results from the coupling of the unsubstituted alkyne C(8) atom of the methyl propynoate molecule to both N atoms of the R-DAB ligand. The substituted alkyne C(13) is σ-bonded to both Fe atoms as a disubstituted μ_2-methylene bridge [Fe(1)–C(13) = 2.004 (4) Å; Fe(2)–C(13) = 2.009 (4) Å]. The Fe(1)–C(13)–Fe(2) angle of 79.4 (2)° and the C(8)–C(13)–C(14) angle of 113.8 (4)° are in the range normally observed for disubstituted μ_2-methylene bridges, as is the relatively short Fe–Fe bond of 2.564 (2) Å.[15] The bond order of the former alkyne

---

[15] Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159.

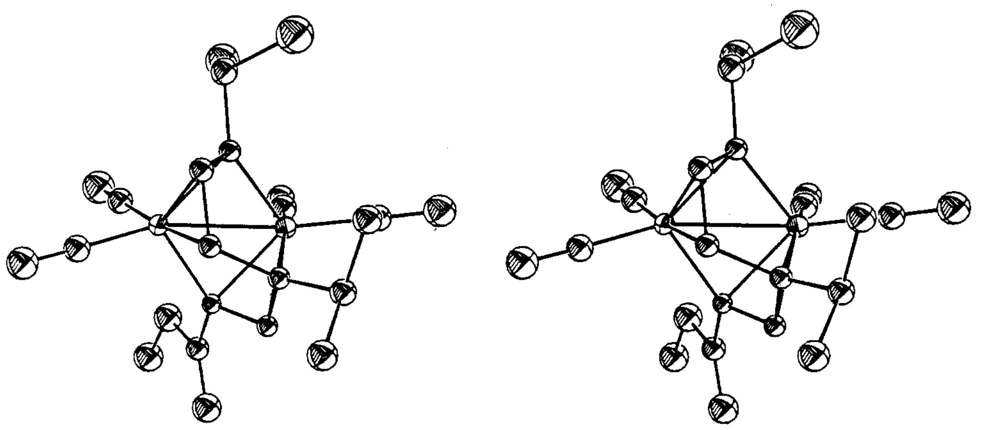
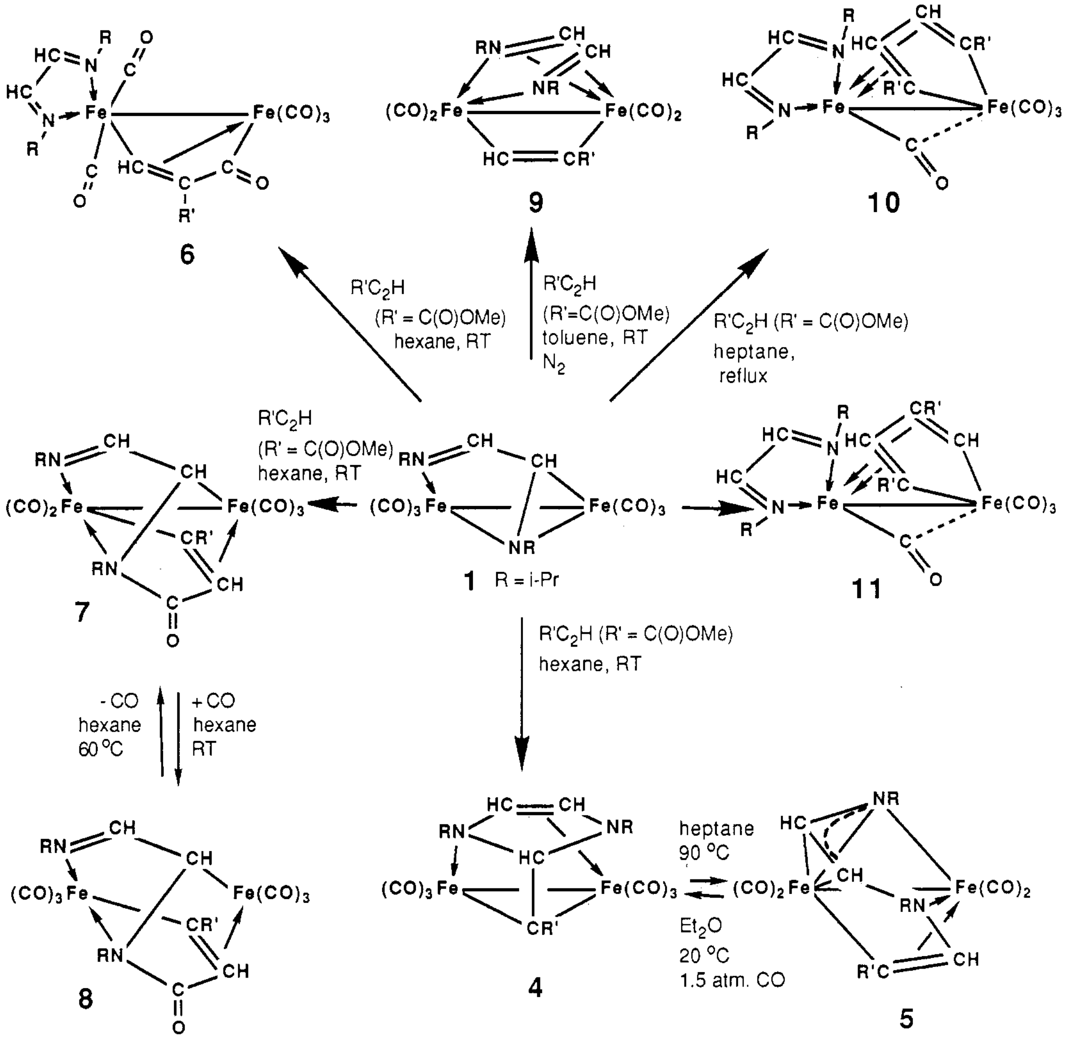


Figure 4. Stereoscopic ORTEP representation of 5 (ellipsoid probability scale 20%).

Scheme I. The Reaction Products of $Fe_2(CO)_6$(*i*-Pr-DAB) with HC≡CR′ [R′ = C(O)OMe]



bond has been reduced from 3 to 1 which is confirmed by the C(8)–C(13) bond length of 1.526 (5) Å. As a consequence the hybridizations of C(8) and C(13) have changed from sp to sp^3 which is in agreement with the average bond angles of 107.8° around C(13) and 109.2° around C(8). The ligand is further bonded to the metal carbonyl core by σ-N-coordination of N(1) to Fe(2) [Fe(2)–N(1) = 2.060 (3) Å] and via the C(9)–Fe(1) bond, which is 2.127 (4) Å long. The C(8)–N(1), C(8)–N(2), and C(9)–N(1) bonds in the ligand have normal bond lengths for a single C–N bond. The C(10)–N(2) bond length of 1.314 (5) Å, however, is too short for a purely single C–N bond,[16] which may indicate that this bond has partly retained its imine nature. The C(9)–C(10) distance of 1.430 (5) Å is also rather short for a single C–C bond and points to a partly double bonding. With respect to the interpretation of these bond lengths in terms of bonding it is noteworthy that fulfillment of the 18-electron rule by Fe(1) requires the donation of two electrons by the cyclic part of the ligand. This conclusion leads to a description of the bonding within the complex as is depicted in Figure 5.

---

[16] Nyburg, S. C. *X-ray Analysis of Organic Compounds*; Academic: New York, 1961.

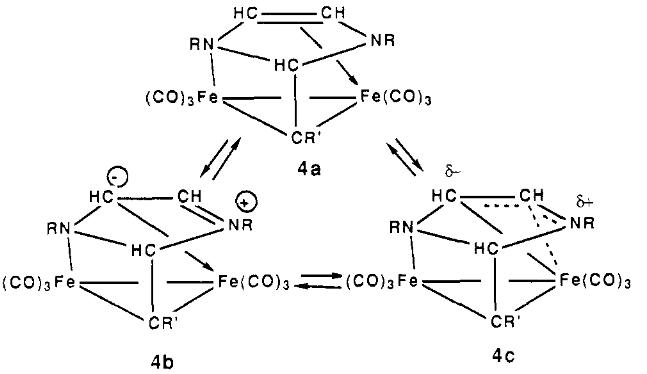


Figure 5. Resonance structures of 4 [R = *i*-Pr, R' = C(O)OMe].

In resonance structure **4b** the imine bond N(2)–C(10) is intact resulting in a positive charge on N(2). C(9), which then carries the corresponding negative charge, is bonded to Fe(1) via a two-electron-donating dative C→Fe bond. Structure **4a** contains a double C(9)–C(10) bond, which is π-bonded to Fe(1). The actual structure **4c** will be closer to **4b** than to **4a**, for η^2-coordination of the double C(9)–C(10) bond would result in a Fe(1)···C(10) distance much shorter than the observed 2.700 (4) Å. We can therefore better describe the C(9)–C(10)–N(2) part of the ligand as an azaallylic fragment, with a partial positive charge localized on N(2) and a partial negative charge on C(9). The bonding of this fragment to Fe(1) then comprises of σ-bond via C(9) as well as a weak π-bonding via the partial double bond C(9)–C(10).

The molecular structure of **5** shows two Fe(CO)$_2$ units linked by a single Fe–Fe bond [Fe(1)–Fe(2) = 2.496 (3) Å] and bridged by a formally 10e-donating organic ligand. The CO ligands are terminally bonded with normal bond lengths and angles. The backbone of the organic ligand consists of the R-DAB NCCN skeleton and the two alkyne C atoms of the methyl propynoate molecule, of which the unsubstituted C(13) atom is coupled to the former imine N(1) atom. The coordination of the ligand to the metal carbonyl core of the complex may be described as follows: N(2) is bonded to both Fe atoms via its lone pair in a μ_2-fashion [Fe(1)–N(2) = 1.999 (10) Å; Fe(2)–N(2) = 1.997 (10) Å], donating two electrons to the Fe$_2$(CO)$_4$ core. The N(2)–C(6)–C(5) part of the ligand forms an azaallyl fragment which, regarded as a neutral fragment, donates three electrons to Fe(2) [C(6)–N(2) = 1.379 (16) Å; C(6)–C(5) = 1.435 (18) Å; C(6)–Fe(2) = 2.035 (13) Å; C(5)–Fe(2) = 2.052 (12) Å]. N(1) is σ-coordinated to Fe(1) and donates two electrons [Fe(1)–N(1) = 1.995 (10) Å] while the former alkyne C(13)–C(14) bond has become π-bonded to Fe(1) and also donates two electrons [Fe(1)–C(13) = 2.039 (11) Å; Fe(1)–C(14) = 2.064 (11) Å]. Finally, C(14) is bonded to Fe(2) via a σ-Fe–C bond [Fe(2)–C(14) = 1.955 (12) Å], formally donating one electron. Describing the N(1)–C(13)–C(14) part of the ligand as a second azaallyl function, as we did in a short communication in which the complex was reported,[5] is probably less appropriate for it would require a partial positive charge on C(14) and a partial negative charge on N(1). This requirement conflicts with the short C(13)–C(14) bond [1.369 (16) Å], which indicates a true double bond. The N(1)–C(13) bond length of 1.434 (15) Å, however, is somewhat short for a single N–C bond, which indicates that there may be some delocalization of electron density in this part of the ligand.

^{1}H and ^{13}C NMR Spectroscopy. The ^{1}H NMR spectrum of **5** shows two doublets due to the former imine protons H(9) and H(10) at 3.75 and 6.70 ppm, respectively. The chemical shift of H(10) is only about 1 ppm upfield with respect to an intact and not π-bonded imine group.[3c] This confirms the above-mentioned conclusion that the imine character of the N(2)–C(10) bond is only slightly affected. The ^{13}C chemical shifts of the corresponding C atoms are 65.2 ppm for C(9) and 101.3 ppm for C(10), which is in agreement with its olefinic character. The former alkyne proton H(8) appears as a very broad signal at 6.58 ppm. The strong broadening of this signal is probably due to quadrupole relaxation caused by the neighboring N atoms. The low-field resonance may be caused by the deshielding effect of the partial positive charge on N(2). In the ^{13}C spectrum C(8) is found at 53.9 ppm, while C(13) resonates at 212.8 ppm. This last resonance is at the end of the range expected for a μ_2-methylene C atom, which is normally found in the range of 100–200 ppm.[15] The methoxy protons appear in the expected range at 3.84 ppm. The ^{1}H and ^{13}C chemical shifts of the isopropyl groups are also found at normal values. The carbonyl C atoms appear as one signal at 212.0 ppm, which suggests a rapid scrambling of the CO's over the Fe$_2$ core. The signals at 212.0 and 212.8 ppm are assigned on basis of their relative intensities.

In the ^{1}H NMR spectrum of **5** H(6) resonates at 6.70 ppm, while H(5) is found at 3.50 ppm. The corresponding C atoms resonate at 75.2 ppm (C(5)) and 113.0 (C(6)). These values are not very different from those found for other azaallyl fragments coordinated to an Fe center.[17] H(13) appears at 6.48 ppm which is normal for a π-bonded olefinic fragment. In the ^{13}C NMR spectrum the olefinic C atoms C(13) and C(14) are found at 114.9 and 169.4 ppm, respectively. The methoxy protons are found as a sharp singlet at 3.89 ppm.

Complex Formation. When 1 and methyl propynoate are stirred in hexane, complex 4 is formed readily at room temperature among a number of other complexes (see Experimental Section). No complexes, however, which can be regarded as intermediates in the formation of 4 could be isolated or even observed spectroscopically. Since the formation of the unusual organic ligand is also to our knowledge unprecedented, it is not directly obvious along which route the reaction has proceeded.

In order to arrive at a likely possibility for a mechanism the following observations and deductions have to be taken into account. First, since both 1 and 4 contain an Fe$_2$(CO)$_6$ core, the intermediates in the reaction should probably also contain six CO ligands. Because no additional CO is necessary for the reaction to proceed and only a limited amount of CO can be anticipated to emerge from decomposition reactions, it is unlikely that Fe$_2$(CO)$_5$ intermediates can react further to Fe$_2$(CO)$_6$ products or that Fe$_2$(CO)$_7$ intermediates are formed and can play a role in the formation of 4. Secondly, in view of the mild reaction conditions it seems not very likely that the mechanism involves extensive rearrangements.

It is worthwhile to regard the possibilities for the initial stage of the reaction mechanism. In the course of the study of reactions of dinuclear metal carbonyl α-diimine complexes with alkynes there are three types of intial reaction steps which are frequently encountered. The first type is the elimination of one CO ligand from M$_2$(CO)$_6$(R-DAB) to give M$_2$(CO)$_5$(R-DAB) with a μ_2-bridging CO and an 8e-donating R-DAB ligand.[18]

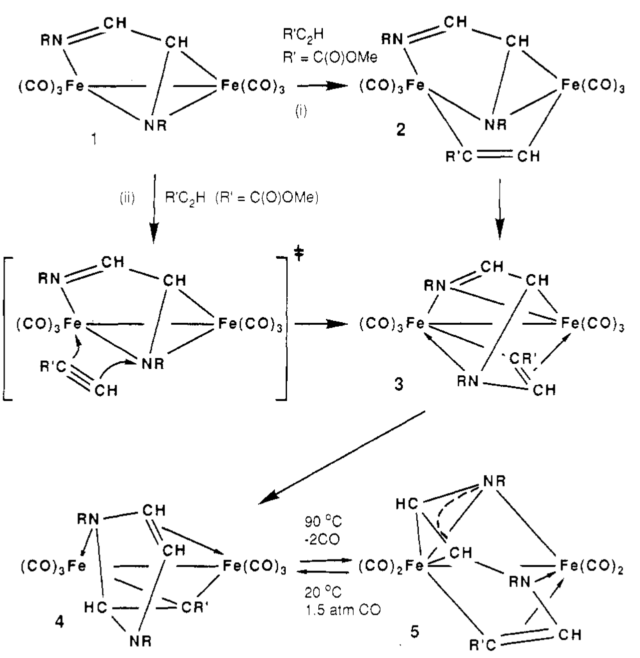
This intermediate can react further with the alkyne via the substitution of the bridging CO by a μ_2-bridging alkyne.

---

[17] Keijsper, J.; Mul, J.; van Koten, G.; Vrieze, K.; Ubbels, H. C.; Stam, C. H. *Organometallics* **1984**, *3*, 1732.

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

Scheme II. Proposed Mechanisms for the Formation of 4 and 5[a]



[a] Compounds 2 and 3 are proposed intermediates.

The second type of initial step is a direct attack of the alkyne on the coordinated imine C atom and the M center to which in $M_2(CO)_6(L)$ (L = R-DAB, R-PYCA) both N atoms of the α-diimine are bonded, to give the $M_2(CO)_6$[AIB] complexes.[19] This reaction takes place mostly when $M_2 = Ru_2$. The third frequently encountered type of initial step is the substitution of the η^2-C=N-coordinated imine moiety of the α-diimine by the monodentate η^2-C≡C-coordinated alkyne. The resulting $M_2(CO)_6(\sigma,\sigma\text{-}L)(\eta^2\text{-alkyne})$ complexes were until now never isolated or observed but are proposed as intermediates in almost all reactions of $Fe_2(CO)_6(L)$ with alkynes.[20]

None of the above-mentioned types of initially formed intermediates, however, is an obvious precursor in the formation of 4. The first type, $M_2(CO)_5$(*i*-PrDAB), would have one CO short. The second type, $M_2(CO)_6$[AIB], was as yet never observed for $M_2 = Fe_2$ while the third type, $Fe_2(CO)_6(\sigma,\sigma\text{-}i\text{-Pr-DAB})(\eta^2\text{-HC}{\equiv}\text{CC(O)OMe})$, contains a chelating DAB ligand, which is not likely to undergo C–N coupling with an alkyne that is coordinated to the other Fe center.

Scheme II shows two possible alternatives. Route (i) involves the insertion of the alkyne in the Fe–Fe bond in 1, resulting in the formation of intermediate 2. The first N–C coupling then occurs between the μ_2-bridging N atom and the alkyne CH moiety resulting in the intermediate complex 3. In route (ii), 3 is the result of a direct attack of the alkyne on the Fe center in 1 to which both N atoms are bonded and the μ_2-N atom of the DAB ligand. In intermediate 3 a second N–C coupling then takes place to give 4. It is difficult, however, to prove which of the mechanistic proposals (i) or (ii) for the formation of intermediate 3 is correct, since neither one of the intermediates 2 and 3 could be detected. We can also not rule out the possibility of the initial substitution of the η^2-C=N-bonded imine in 1 by an alkyne molecule, after which an intramolecular attack of one of the imine fragment on the coordinated alkyne results in the first C–N coupling.

Only two other examples are known in which both N atoms of a R-DAB molecule are coupled to the same C atom. One is the Fe catalyzed formation of imidazolone in the reaction of $Fe_2(CO)_9$ with R-DAB in CO atmosphere.[21] In this reaction the nucleophilic attack of the uncoordinated imine N atom of a monodentate σ-N coordinated R-DAB in $Fe(CO)_4$(R-DAB) to one of the CO ligands yields $(CO)_3Fe[N(R)C(H){=}C(H)N(R)C(O)]$. Addition of a subsequent R-DAB or CO ligand results in ring closure to form the imidazolone, which finally is easily displaced from the Fe center by coordination of further R-DAB or CO ligands. The second example, recently reported by tom Dieck et al.,[22] is the reaction of two equivalents of R-DAB with dry HCl, resulting in N,N'-dialkylimidazolonium salts with the concomitant formation of the corresponding ammonium salts RNH_3Cl.

The thermal rearrangement of 4 to 5 obviously involves the fission of one of the C–N bonds between the R-DAB and the alkyne and concomitant loss of two CO ligands. It is not possible to prove unambiguously which one of the N–C bonds is broken, for in both cases the same ligand would be obtained. The most likely possibility, however, seems to be the fission of the N(2)–C(8) bond. In this case the N(2)–C(9)–C(10) part of the ligand would form the η^3-bonded azaallyl function present in 5, which seems reasonable in view of the already partial azaallylic nature of this fragment in 4. Also in this case N(1) would retain its σ-N bonding to Fe(2). The single C(8)–C(13) bond in 4 becomes in this process a double bond. The σ-Fe–C bond between Fe(2) and C(13) in 4 is hence replaced by the resulting π-coordinated olefinic fragment. This is in agreement with the already short C(8)···Fe(2) distance of 2.545 (3) Å in 4. A less likely possibility comprises the rearrangement of 4 to 5 after the fission of the N(1)–C(8) bond that, however, would require the formation of an N(1)–C(9)–C(10) azaallyl function and the complete reduction of the N(2)–C(10) bond to a single bond.

Attempts to shed more light on the mechanism discussed above by using asymmetrically substituted DAB ligands were not successful: The reaction of methyl propynoate with $Fe_2(CO)_6$[*i*-Pr-DAB(H,Me)],[3c] in which the proton on the σ-N-coordinated imine group is substituted by a methyl group, did not yield a product of type 4. Reaction of $Fe_2(CO)_6$[*i*-Pr-N=C(H)C(H)=N-*t*-Bu][23] in which the N atoms have different substituents with methyl propynoate yielded not more than a minor amount of the asymetrically N,N'-disubstituted analogue of 4, for which, however, it was not possible to determine to which N atom the *i*-Pr or *t*-Bu group was bonded.

Also for the CO-induced reverse reaction of 5 to 4 it appeared to be very difficult to assess with some certainty a likely mechanism. We could, however, anticipate that addition of one or two CO ligands to the Fe carbonyl core of 5 would result in an intermediate in which N(2) and C(13) are brought in close proximity to the effect that the N–C coupling to give 4 could take place.

The $Fe_2(CO)_6$(*i*-Pr-DAB)/Methyl Propynoate Reaction (Scheme I). In this paper and the previous two parts of this series,[6,18] we have described the isolation and characterization of the major products of the reaction of

---

[19] 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 RN=CHCH(NR)C(R')=CR'', which is 2-amino-4-imino-1-butene.[3a]

[20] Muller, F.; Vrieze, K. In *Coordination Chemistry and Catalysis*; Ziolkowski, J. J., Ed.; World Scientific Publishing Co.: Singapore, 1988.

[21] Staal, L. H.; Polm, L. H.; Vrieze, K. *Inorg. Chim. Acta* **1980**, *40*, 165.

[22] Zettlitzer, M.; tom Dieck, H.; Haupt, E. T. K.; Stamp, L. *Chem. Ber.* **1986**, *119*, 1868.

[23] Frühauf, H.-W.; Breuer, J. *J. Organomet. Chem.* **1986**, *310*, 183.

$Fe_2(CO)_6$(*i*-Pr-DAB) with methyl propynoate at room temperature. The complexes $Fe_2(CO)_n$[(*i*-Pr)N=CHCHN(*i*-Pr)C(O)CH=CC(O)OMe] (7, $n = 5$; 8, $n = 6$) are discussed in part 2 and contain a flyover-type ligand resulting from the coupling of a MeOC(O)C=CHC(O) fragment to one of the DAB N atoms.[6] They are formed in a total yield of about 50% with a varying 7/8 ratio. The pentacarbonyl complex 7 can easily and reversibly be converted into the hexacarbonyl complex 8 by reaction with CO. The third major product $Fe_2(CO)_6$[(*i*-Pr)-NCH=CHN(*i*-Pr)CHCC(O)OMe] (4) and its thermal and reversible transformation into $Fe_2(CO)_4$[(*i*-Pr)NCHCHN-(*i*-Pr)CH=CC(O)OMe] (5) are discussed in this paper. The complex $Fe_2(CO)_5$(*i*-Pr-DAB)[μ_2-HC=C(C(O)OMe)-C(O)] (6), which will be discussed in part 5 of this series,[19] can be isolated as a minor product from the reaction of $Fe_2(CO)_6$(*i*-Pr-DAB) with methyl propynoate. Its isolation confirmed our idea that an isomeric complex, with the alkyne CH and CC(O)Me moieties interchanged, is intermediate in the formation of the flyover complexes 7 and 8. When the reaction mixture of $Fe_2(CO)_6$(*i*-Pr-DAB) and methyl propynoate is purged with N_2, the complex $Fe_2(CO)_4$(*i*-Pr-DAB)(μ_2-HC≡CC(O)OMe) (9) is formed in good yield. The required reaction conditions indicate that its formation proceeds via the intermediate $Fe_2(CO)_5$(*i*-Pr-DAB), which was as yet never isolated or observed. This is discussed in part 1 of this series.[18] Finally, at higher reaction temperatures the main products of the reaction of $Fe_2(CO)_6$(*i*-Pr-DAB) with methyl propynoate are the complexes $Fe_2(CO)_4$(*i*-Pr-DAB)[MeOC(O)C=CHCH=CC(O)OMe] (10) and $Fe_2(CO)_4$(*i*-Pr-DAB)[MeOC(O)C=CHC(C(O)OMe)=CH] (11), which are formed via the tail-to-tail and head-to-tail coupling, respectively, of two alkyne molecules. Their formation, structure, and properties will be discussed in part 4 of this series.[9] The above-mentioned products are shown in scheme I.

It has become clear that a number of the above-mentioned products are formed simultaneously in the same reaction and that the employed reaction conditions have a large influence on which reaction path is chosen. These observations are indicative for the small differences between the activation barriers of the different reaction routes leading to the different products. The great variety of novel complexes resulting from the reactions of $Fe_2(CO)_6$(*i*-Pr-DAB) and methyl propynoate is no doubt related to the steric and electronic properties of this alkyne, since similar reactions with other alkynes, e.g. MeOC(O)C≡CC(O)OMe, HC≡CH, and PhC≡CH, produce a much smaller number of products.

The flyover complexes 7 and 8 are of potential interest from an organic point of view since the isostructural "classical" flyover complexes M_2L_n[RC=CRC(O)CR=CR] resulting from the coupling of two alkyne molecules to a CO in reactions of metal carbonyls with alkynes are known as precursors in the formation of various heterocyclic organic compounds. A similar conclusion holds for complexes 4 and 5. Isolation of the heterocyclic ligand present in 4, for example, by protonation of the μ_2-methylene bridge, would provide an interesting synthetic route to *N*,*N'*-dialkyldiazolines. The structural similarity of the ligand in 5 to the bis(allyl) ligands in complexes M_2L_n-(alkyne)$_3$, which are regarded as possible intermediates in the formation of benzene derivates,[24,25] suggests the possibility of the formation of heterocyclic compounds via the ring closure of the ligand.

Conclusions

We have shown that reactions of unsaturated organic molecules with η^2-C=N coordinated R-DAB ligands are not limited to C—C coupling reactions, of which many examples are now known, but may also lead to various N—C coupled products. We have no absolute certainty about the mechanism of the formation of 4, although it is most likely that the N–C coupling reactions do not occur simultaneously and that the involved intermediates all contain an $Fe_2(CO_6$ core. Since such a double N–C coupling of an α-diimine with an alkyne is to our knowledge unprecedented, there are no known reactions to be compared. The same holds for the reversible transformation of 4 into 5, although it is not unlikely that the transformation of 4 into 5 proceeds via the fission of the N(2)–C(8) bond.

This thermally induced reversible reaction of 4 to give 5 shows that not only N–C bond formation but also N–C bond cleavage may be important processes in the reactions of coordinated α-diimine ligands with unsaturated substrates on dinuclear iron carbonyl moieties.

Acknowledgment. J. M. Ernsting is thanked for assisting in measuring the ^{13}C NMR spectra. The Institute for Mass Spectrometry of the University of Amsterdam is thanked for measuring the field-desorption mass spectra. Dr. H.-W. Frühauf and Dr. C. J. Elsevier are thanked for critically revising the manuscript.

Registry No. **1**, 74552-74-2; **4**, 104389-73-3; **5**, 104426-24-6; **6**, 117119-49-0; **7**, 104407-18-3; **8**, 117119-50-3; **10**, 104390-09-2; **11**, 117119-51-4; MeOC(O)C_2H, 922-67-8; Fe(CO)$_3$(iPr-DAB), 54446-62-7; Fez(CO)$_6$[*i*-Pr-DAB(H,Me)], 74552-75-3; Fez(CO)$_6$-[*i*-Pr-N=C(HC(H)=N-*t*-Bu] (isomer I), 106108-77-4; Fez-(CO)$_6$[*i*-Pr-N=C(HC(H)=N-*t*-Bu] (isomer II), 106108-76-3; 1,3,5-tris(methoxycarbonyl)benzene, 2672-58-4; 1,2,4-tris(methoxycarbonyl)benzene, 2459-10-1.

Supplementary Material Available: Tables of anisotropic thermal parameters of the non-hydrogen atoms, the calculated fractional coordinates of the H atoms, and the bond angles of the non-hydrogen atoms for 4 and tables of the anisotropic thermal parameters of the Fe atoms and bond angles for 5 (5 pages); listings of structure factor amplitudes for 4 and 5 (37 pages). Ordering information is given on any current masthead page.

---

(24) Mills, O. S.; Robinson, G. *Proc. Chem. Soc.* **1974**, 187.

(25) Knox, S. A. R.; Stansfield, R. F. D.; Stone, F. G. A.; Winter, M. J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1978**, 221.