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C–C and C–N Couplings and Alkyl C–H Activation in Reactions of (σ,σ(N,N′)-*N*,*N*′-Diisopropyl-1,4-diaza-1,3-butadiene)-(μ_2,η^2-dimethyl acetylenedicarboxylate)diiron Pentacarbonyl[1,2]

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$Fe_2(CO)_6$(*i*-Pr-DAB) (1) reacts at 20 °C with dimethyl acetylenedicarboxylate to give $Fe_2(CO)_5$(*i*-Pr-DAB)[μ_2,η^2-MeOC(O)C≡CC(O)OMe] (3). The X-ray crystal structure of 3, which is fluxional in solution, shows a 4e donating σ,σ-N,N′ chelating DAB ligand. A μ_2,η^2-perpendicular bridging alkyne, a semibridging CO ligand, and a single Fe–Fe bond of 2.5628 (16) Å connect the Fe(DAB)(CO) and $Fe(CO)_3$ fragments, which contain terminally bonded CO ligands. Dark purple crystals of 3, $Fe_2C_{19}H_{22}N_2O_9$ (M = 534.08), belong to the space group *Pbca* and have cell constants a = 16.223 (4) Å, b = 18.240 (5) Å, c = 15.809 (4) Å, and Z = 8. A total of 2502 reflections (Mo Kα, μ = 12.86 cm^{-1}) have been used in the refinement resulting in a final R value of 0.071 (R_w = 0.132). Complex 3 reacts at 20 °C with R′C≡CC(O)OMe [R′ = H, C(O)OMe] to give the ferracyclopentadienyl complexes Fe_2[MeOC(O)C=CR′C(C(O)OMe)=CC(O)OMe]$(CO)_4$(*i*-Pr-DAB) (4a,b). When 3 is treated at 20 °C with CO, the flyover complex $Fe_2(CO)_5$[*i*-PrN=CHCHN-(*i*-Pr)C(O)C(C(O)OMe)=CC(O)OMe] (9), resulting from the coupling of one of the DAB N atoms and an alkyne C atom to a CO molecule, is formed. Complex 9 reacts reversibly with CO to give $Fe_2(CO)_6$-[*i*-PrN=CHCHN(*i*-Pr)C(O)C(C(O)OMe)=CC(O)OMe] (10). Finally, at 60 °C 3 undergoes a very unusual thermally induced isomerization yielding two orange products (6, 7) which one of the methine protons of the DAB ligand has migrated to the alkyne. The structure of $Fe_2(CO)_5$[Me_2C=N-CHCHN-*i*-Pr][η^1-MeOC(O)C=CHC(O)OMe] (7) is confirmed by an X-ray crystal structure determination. Dark orange crystals of 7, $Fe_2C_{19}H_{22}N_2O_9$ (M_r = 534.08), belong to the space group $P\bar{1}$ and have cell constants a = 14.683 (1) Å, b = 16.731 (1) Å, c = 9.659 (1) Å, α = 94.86 (1)°, β = 90.77 (1)°, γ = 88.10 (1)°, and Z = 4. The refinement of 3176 absorption-corrected reflections (Cu Kα, μ = 103.3 cm^{-1}) have been used in the refinement resulting in a final R value of 0.056 (R_w = 0.085). In complex 7 the vinyl fragment is η^1-bonded to the Fe atom to which the Me_2C=N moiety of the ligand is σ-N coordinated. The other part of the ligand is bonded as an azaallyl fragment to the other Fe atom. The molecular structure further shows a single Fe–Fe bond [2.583 (2) Å] and terminally bonded CO ligands. In $Fe_2(CO)_5$[Me_2C=NCHCH=N-*i*-Pr][μ_2,η^2-MeOC-(O)C=CHC(O)OMe] (6) the H migration resulted in a μ_2,η^2-vinyl fragment, which is σ-bonded to that Fe atom to which both N atoms are coordinated. The former imine C atom is σ-bonded to the other Fe center.

Introduction

α-Diimine ligands in transition-metal complexes are known to show a very versatile coordination behavior, resulting from the possibility of donating from two to eight electrons via the N lone pairs and the C=N π-electrons to the metal center(s) to which they are bonded.[3] Also the reactivity of the various formed α-diimine complexes toward small (organic) molecules appeared to be of great interest.[4] Of the known dinuclear α-diimine carbonyl complexes, the reactivity of $Ru_2(CO)_6$(R-DAB)[4d] [R-DAB = 1,4-diaza-1,3-butadiene, RN=CHCH=NR] has been studied most extensively. The reactivity of this complex, in which the α-diimine ligand is bonded as a σ-N,μ_2-N′,η^2-C=N′ six-electron donor, toward unsaturated organic molecules is dominated by C–C coupling reactions of the coordinated imine C atom and one of the unsaturated C atoms of the organic substrate. Examples are reactions with R-DAB itself,[4d] sulfines (R_2C=S=O),[4f] carbodiimides (RN=C=NR),[4f] and alkynes.[4e] Reactions of $Ru_2(CO)_6$-(R-DAB) with alkynes resulted in a number of interesting organometallic species, originating from C–C bond formation reactions.[4e]

These results stimulated us to direct our attention to the other members of the $M_2(CO)_6$(L) group[5] [M_2 = Fe_2, FeRu, Ru_2; L = R-DAB, R-Pyca (= pyridine-2-carbaldimine)] toward acetylene and substituted alkynes. An important goal of this study is to obtain greater knowledge of the initial steps in the reactions of $M_2(CO)_6$(L) with alkynes.

In this paper we present the crystal structure and reactivity of $Fe_2(CO)_5$(*i*-Pr-DAB)[μ_2,η^2-MeOC(O)C≡CC-

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(1) Reactions of Dinuclear Metal Carbonyl α-Diimine Complexes with Alkynes. 6. For part 5: see ref 2.

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Table I. IR and Mass Spectroscopic Data and Elemental Analyses of $\mathrm{Fe_2(CO)_5}$(*i*-Pr-DAB)[μ_2,η^2-MeOC(O)C$\equiv$CC(O)OMe] (3), $\mathrm{Fe_2(CO)_5}$[$\mathrm{Me_2C{=}NCHCH{=}N}$-*i*-Pr][$\mu_2,\eta^2$-MeOC(O)C=CHC(O)OMe] (6), $\mathrm{Fe_2(CO)_5}$[$\mathrm{Me_2C{=}NCHCHN}$-*i*-Pr][η^1-MeOC(O)C=CHC(O)OMe] (7), $\mathrm{Fe_2(CO)_5}$[*i*-PrN=CHCHN(*i*-Pr)C(O)C(C(O)OMe)=CC(O)OMe] (9), and $\mathrm{Fe_2(CO)_6}$[*i*-PrN=CHCHN(*i*-Pr)C(O)C(C(O)OMe)=CC(O)OMe] (10)

			elemental analysis					
			C		H		N	
compd	FD mass	IR ν(C=O),[b] cm^{-1}	obsd	calcd	obsd	calcd	obsd	calcd
3	534 (534.08)	2050 (s), 2003 (s), 1994 (m), 1895 (m), 1707 (m)[c]	41.78	42.73	4.07	4.15	5.15	5.25
6	534 (534.08)	2038 (s), 1998 (s), 1975 (s, b), 1700 (s)[d]	41.14	42.73	4.14	4.15	4.99	5.25
7	534 (534.08)	2044 (s), 1998 (s), 1975 (s), 1960 (sh), 1702 (s)[d]	41.67	42.73	4.21	4.15	4.96	5.25
9	562 (562.10)	2074 (s), 2010 (vs), 1976 (s), 1712 (m), 1675 (w)[c]	42.95	42.74	4.32	3.94	4.80	4.98
10	562 (590.11)	2090 (s), 2043 (vs), 1980 (s), 1952 (s), 1729 (s), 1672 (m)[d]	42.1	42.74	3.8	3.76	4.6	4.75

[a] Calculated values in parentheses. Based on ^{56}Fe. [b] Abbreviations: s, strong; m, medium; w, weak; b, broad; sh, shoulder. [c] In hexane solution. [d] In dichloromethane solution.

Table II. ^{1}H NMR Data of $\mathrm{Fe_2(CO)_5}$(*i*-Pr-DBA)[μ_2,η^2-MeOC(O)C$\equiv$CC(O)OMe] (3), $\mathrm{Fe_2(CO)_5}$[$\mathrm{Me_2C{=}NCHCH{=}N}$-*i*-Pr][$\mu_2,\eta^2$-MeOC(O)C=CHC(O)OMe] (6), $\mathrm{Fe_2(CO)_5}$[$\mathrm{Me_2C{=}NCHCHN}$-*i*-Pr][η^1-MeOC(O)C=CHC(O)OMe] (7), $\mathrm{Fe_2(CO)_5}$[*i*-PrN=CHCHN(*i*-Pr)C(O)C(C(O)OMe)=CC(O)OMe] (9), and $\mathrm{Fe_2(CO)_6}$[*i*-PrN=CHCHN(*i*-Pr)C(O)C(C(O)OMe)=CC(O)OMe] (10)[a]

compd	*i*-Pr Me	*i*-Pr CH	N–CH	C(O)OMe
3[b]	1.10/1.14 (6 H, d/d, 7 Hz)	3.82, 4.38 (2 × 1 H, sept, 7 Hz)	7.73, 7.82 (2 × 1 H, s)	3.49, 3.75 (2 × 3 H, s)
	1.33 (6 H, d, 7 Hz)			
6	1.23/1.29 (6 H, d/d, 6.5 Hz)	4.16 (1 H, sept, 6.5 Hz)	7.96 (1 H, d, 1.5 Hz)	3.66, 3.70 (2 × 3 H, s)
	1.73, 2.19 (2 × 3 H, s)	6.09 (1 H, s; C=CH)	3.61 (1 H, d, 1.5 Hz)	
7	1.58/1.80 (6 H, d/d, 6.5 Hz)	4.12 (1 H, sept, 6.5 Hz)	6.73 (1 H, d, 2 Hz)	3.63, 3.84 (2 × 3 H, s)
	1.97, 2.09 (2 × 3 H, s)	5.18 (1 H, s; C=CH)	4.50 (1 H, d, 2 Hz)	
9	1.10/1.25 (6 H, d/d, 7 Hz)	3.11, 3.62 (2 × 1 H, sept, 7 Hz)	7.89 (1 H, d, 1.5 Hz)	3.72, 3.81 (2 × 3 H, s)
	1.41 (6 H, d, 7 Hz)		2.84 (1 H, d, 1.5 Hz)	
10[c]	1.17/1.22 (6 H, d/d, 7 Hz)	2.88, 3.71 (2 × 1 Hz, sept, 7 Hz)	8.12 (1 H, d, 2 Hz)	3.75 (6 H, s)
	1.36/1.39 (6 H, d/d, 7 Hz)		3.20 (1 H, d, 2 Hz)	

[a] Values in ppm relative to TMS, measured in $\mathrm{CDCl_3}$ solution at 293 K; spectrometer frequency = 100 MHz. [b] Slow-exchange limit, T = 263 K. [c] Spectrometer frequency = 250 MHz.

Table III. ^{13}C NMR Data of $\mathrm{Fe_2(CO)_5}$(*i*-Pr-DAB)[μ_2,η^2-MeOC(O)C$\equiv$CC(O)OMe] (3), $\mathrm{Fe_2(CO)_5}$[$\mathrm{Me_2C{=}NCHCH{=}N}$-*i*-Pr][$\mu_2,\eta^2$-MeOC(O)C=CHC(O)OMe] (6), $\mathrm{Fe_2(CO)_5}$[$\mathrm{Me_2C{=}NCHCHN}$-*i*-Pr][η^1-MeOC(O)C=CHC(O)OMe] (7), $\mathrm{Fe_2(CO)_5}$[*i*-PrN=CHCHN(*i*-Pr)C(O)C(C(O)OMe)=CC(O)OMe] (9), and $\mathrm{Fe_2(CO)_6}$[*i*-PrN=CHCHN(*i*-Pr)C(O)C(C(O)OMe)=CC(O)OMe] (10)[a]

compd	*i*-Pr Me	*i*-Pr CH	N–CH	C≡C	C(O)O	OMe	N–C(O)	CO
3	22.6, 23.3, 25.8 (2×)	58.8, 62.8	149.2, 153.5	74.3, 86.5	170.2, 175.0	52.1, 52.8		206.3, 209.5, 214.2, 233.5
6	24.0, 24.1, 28.0, 31.6[b]	58.8, 161.7[c]	169.6, 73.2	101.2	178.0, 180.3	51.7, 51.8		209.8, 216.5
				125.4				
7	22.6, 24.3, 28.9, 30.6[b]	64.5, 161.3[c]	123.4, 71.5	171.0	179.4, 186.4	51.6, 51.7		211.7, 213.0, 216.0
				99.6				
9	18.6, 18.7, 22.3, 23.2	55.1, 61.1	175.4, 26.7	166.4	167.2, 176.1	52.3, 52.6	178.5	204.6, 206.7, 212.7, 213.0, 215.1
				63.2				
10	18,9, 22.7, 23.1, 23.5	56.2, 60.9	171.8, 51.2	97.3	170.5, 177.1	51.6, 52.3	179.7	201.8, 202.6, 206.8, 209.8
				62.3				

[a] Values in ppm, relative to $\mathrm{Me_4Si}$, measured in $\mathrm{CDCl_3}$ solution, spectrometer frequency 25 MHz, T = 263 K. [b] N=C($\mathrm{CH_3}$)$_2$. [c] N=*C*($\mathrm{CH_3}$)$_2$.

(O)OMe] (**3**), which is one of the products that can be isolated from the reaction of $\mathrm{Fe_2(CO)_6}$(*i*-Pr-DAB) (**1**) with dimethyl acetylenedicarboxylate (DMADC).[6] The reactivity of **3**, e.g. toward DMADC or CO or upon heating, appeared to depend strongly on the experimental conditions and involves C–C and C–N coupling processes and alkyl C–H activation. The crystal structure is reported of one of the products resulting from such a C–H activation, i.e. $\mathrm{Fe_2(CO)_5}$[$\mathrm{Me_2C{=}NCHCHN}$-*i*-Pr][η^1-MeOC(O)C=CHC(O)OMe] (**7**).

Experimental Section

Materials and Apparatus. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC100 and WM250 spectrometers. IR spectra were measured with a Perkin-Elmer 283 spectrometer. FD mass spectra were obtained on a Varian MAT711 double-focussing 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. $\mathrm{Fe_2(CO)_5}$(*i*-Pr-DAB)[μ_2,η^2-MeOC(O)C$\equiv$CC(O)OMe] (**3**) and $\mathrm{Fe_2}$[MeOC(O)C=CR′C(C(O)OMe)=CC(O)OMe]$\mathrm{(CO)_4}$(*i*-Pr-DAB) (**4a**, R′ = C(O)OMe; **4b**, R′ = H) were prepared according to known procedures.[6] Carbon monoxide was used as commercially obtained without further purification. The products were identified by IR and mass spectrometry, by elemental analyses (Table I) and by ^{1}H (Table II) and ^{13}C NMR (Table III).

Thermal Isomerization of $\mathrm{Fe_2(CO)_5}$(*i*-Pr-DAB)[μ_2,η^2-MeOC(O)C$\equiv$CC(O)OMe] (3) to $\mathrm{Fe_2(CO)_5}$[$\mathrm{Me_2C{=}NCHCH{=}N}$-*i*-Pr][$\mu_2,\eta^2$-MeOC(O)C=CHC(O)OMe] (6) and $\mathrm{Fe_2(CO)_5}$[$\mathrm{Me_2C{=}NCHCHN}$-*i*-Pr][η^1-MeOC(O)C=CHC(O)-

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(6) 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* 1989, *158*, 81.

Table IV. Crystallographic Data for $Fe_2(CO)_5$(*i*-Pr-DAB)[μ_2,η^2-MeOC(O)C≡CC(O)OMe] (3) and $Fe_2(CO)_5[Me_2C$=NCHCHN-*i*-Pr][η^1-MeOC(O)C=CHC(O)OMe] (7)

	3	7
formula, mol wt	$Fe_2C_{19}H_{22}N_2O_9$, 534.08	$Fe_2C_{19}H_{22}N_2O_9$, 534.08
cryst system	orthorhombic	triclinic
space group	*Pbca*	$P\bar{1}$
a, Å	16.223 (4)	14.683 (1)
b, Å	18.240 (5)	16.731 (1)
c, Å	15.809 (4)	9.659 (1)
α, deg	90	94.86 (1)
β, deg	90	90.77 (1)
γ, deg	90	88.10 (1)
V, $Å^3$	4677	2363
d_{calcd}, $g\cdot cm^{-3}$	1.51; 8	1.502; 4
μ, cm^{-1}	12.86	103.3
cryst color, size, mm^3	purple, 0.43 × 0.40 × 0.1	dark orange, 0.25 × 0.50 × 0.04
radiatn	Mo Kα, λ = 0.710 69 Å	Cu Kα, λ = 1.5418 Å
2θ range, deg	2.2–60	5.3–110
no. of reflctns	7427	5916
no. with $I < 2.5\sigma(I)$	4925	2739
no. of reflctns in refinement	2502	3176
h min, max	0, 22	−15, 14
k min, max	0, 25	−17, 17
l min, max	0, 21	−2, 10
abs corr	no	DIFABS
extinctn corr	isotropic	no
weighting scheme	$w = 1/(4.5 + F_o + 0.036F_o^2)$	$w = 1/(8.94 + F_o + 0.0185F_o^2)$
anomalous scattering	Fe	Fe
final *R*, R_w	0.071, 0.132	0.056, 0.085

OMe] (7). A solution of **3** (0.8 mmol, 429 mg) in 40 mL of toluene was heated to 60 °C for 1.5 h. The color of the solution changed from purple to orange-brown. The reaction mixture was separated by column chromatography. A small amount of **9** was obtained by elution with hexane/diethyl ether (2:3). Elution with diethyl ether yielded an orange solution from which after evaporation of the solvent **6** was isolated (80 mg, 21% yield). Further elution with diethyl ether produced an orange-yellow fraction containing **7**. Concentrating this fraction to 30 mL and cooling to −30 °C produced dark orange crystals suitable for X-ray crystallography that were collected by decanting the supernatant solution and were dried in vacuo (177 mg, 41% yield).

Synthesis of $Fe_2(CO)_5$[*i*-PrN=CHCHN(*i*-Pr)C(O)C(C(O)OMe)=CC(O)OMe] (9). Method A. A solution of **3** (1 mmol, 534 mg) in 50 mL of diethyl ether was stirred under 1.5 atm of CO for 16 h, during which the intensely purple color of the solution changed to orange-yellow. The reaction mixture was evaporated to dryness, and the crude product was purified by column chromatography. Compound **9** was obtained by elution with hexane/diethyl ether (2:3) in 60% yield and was recrystallized from hexane/diethyl ether (2:1) at −80 °C.

Method B. A solution of $Fe_2(CO)_6$[*i*-PrN=CHCHN(*i*-Pr)C(O)C(C(O)OMe)=CC(O)OMe] (**10**, vide infra) (0.5 mmol, 245 mg) in 50 mL of heptane/dichloromethane (1:1) was purged with N_2 at 20 °C for about half an hour, during which the orange-yellow color of the solution gradually changed to brown. The reaction was stopped when the IR spectrum of the reaction mixture (ν_s(C=O) region 1600–2200 cm^{-1}) the bands of **10** were replaced by those of **9**. The obtained solution was concentrated to 20 mL and cooled to −80 °C. The precipitated complex **9** could be isolated in >95% yield by decanting the supernatant solution and was dried in vacuo.[7]

Synthesis of $Fe_2(CO)_6$[*i*-PrN=CHCHN(*i*-Pr)C(O)C(C(O)OMe)=CC(O)OMe] (10). A solution of **9** (0.5 mmol, 231 mg) in 50 mL of hexane/dichloromethane (4:1) was purged with CO at 20 °C. Almost immediately the brown color changed to orange-yellow. After 5 min the reaction was completed as was shown by the absence of the bands of **9** in the IR spectrum of the reaction mixture (ν_s(C=O) region 1600–2200 cm^{-1}) which were replaced by those of **10**. Complex **10** could be isolated in quantitative yield by concentrating the solution to 30 mL and subsequent cooling to −80 °C. The supernatant solution was decanted and the formed orange crystals were dried in vacuo.

Table V. Selected Bond Lengths (Å) of the Non-Hydrogen Atoms of 3 (Esd's in Parentheses)

Fe(1)–Fe(2)	2.5628 (16)	C(2)–O(2)	1.168 (10)
Fe(1)–C(2)	1.804 (8)	C(6)–C(7)	1.344 (10)
Fe(1)–C(6)	1.974 (7)	C(6)–C(10)	1.485 (10)
Fe(1)–C(7)	2.019 (7)	C(7)–C(8)	1.484 (9)
Fe(1)–N(1)	1.930 (6)	C(12)–C(13)	1.429 (11)
Fe(1)–N(2)	1.981 (6)	C(12)–N(1)	1.300 (9)
Fe(2)–C(2)	2.337 (8)	C(13)–N(2)	1.302 (9)
Fe(2)–C(6)	1.960 (7)	C(14)–N(2)	1.498 (10)
Fe(2)–C(7)	1.944 (7)	C(17)–N(1)	1.481 (10)

Table VI. Selected Bond Angles (deg) of the Non-Hydrogen Atoms of 3 (Esd's in Parentheses)

Fe(2)–Fe(1)–C(2)	61.8 (3)	Fe(1)–C(2)–O(2)	159.5 (6)
Fe(2)–Fe(1)–C(6)	49.1 (2)	Fe(2)–C(2)–O(2)	125.2 (7)
Fe(2)–Fe(1)–C(7)	48.4 (2)	Fe(1)–C(6)–Fe(2)	81.3 (4)
Fe(2)–Fe(1)–N(1)	142.3 (2)	Fe(1)–C(6)–C(7)	72.2 (6)
Fe(2)–Fe(1)–N(2)	112.4 (2)	Fe(1)–C(6)–C(10)	135.7 (5)
C(2)–Fe(1)–C(6)	107.6 (5)	Fe(2)–C(6)–C(7)	69.2 (7)
C(2)–Fe(1)–C(7)	105.0 (5)	Fe(2)–C(6)–C(10)	131.5 (6)
C(2)–Fe(1)–N(1)	155.8 (3)	C(7)–C(6)–C(10)	140.2 (7)
C(2)–Fe(1)–N(2)	89.0 (4)	Fe(1)–C(7)–Fe(2)	80.5 (4)
C(6)–Fe(1)–C(7)	39.3 (3)	Fe(1)–C(7)–C(6)	68.5 (6)
C(6)–Fe(1)–N(1)	95.5 (4)	Fe(1)–C(7)–C(8)	128.2 (5)
C(6)–Fe(1)–N(2)	132.3 (3)	Fe(2)–C(7)–C(6)	70.5 (6)
C(7)–Fe(1)–N(1)	97.2 (4)	Fe(2)–C(7)–C(8)	138.6 (5)
C(7)–Fe(1)–N(2)	93.7 (4)	C(6)–C(7)–C(8)	142.3 (6)
N(1)–Fe(1)–N(2)	80.1 (4)	C(13)–C(12)–N(1)	114.6 (8)
Fe(1)–Fe(2)–C(2)	42.9 (2)	C(12)–C(13)–N(2)	114.7 (9)
Fe(1)–Fe(2)–C(6)	49.6 (3)	Fe(1)–N(1)–C(12)	116.1 (6)
Fe(1)–Fe(2)–C(7)	51.0 (2)	Fe(1)–N(1)–C(17)	126.3 (5)
C(2)–Fe(2)–C(6)	90.1 (4)	C(12)–N(1)–C(17)	117.6 (8)
C(2)–Fe(2)–C(7)	89.9 (4)	Fe(1)–N(2)–C(13)	114.2 (6)
C(6)–Fe(2)–C(7)	40.3 (3)	Fe(1)–N(2)–C(14)	127.8 (5)
Fe(1)–C(2)–Fe(2)	75.3 (5)	C(13)–N(2)–C(14)	117.8 (8)

Crystal Structure Determinations of $Fe_2(CO)_5$(*i*-Pr-DAB)[μ_2,η^2-MeOC(O)C≡CC(O)OMe] (3) and $Fe_2(CO)_5[Me_2C$=NCHCHN(*i*-Pr)][η^1-MeOC(O)C=CHC(O)OMe] (7). The crystal data, X-ray data collection parameters, and refinement data for **3** and **7** are listed in Table IV.

The reflections were measured on a Nonius CAD4 diffractometer (20 °C, θ–2θ scan). Those with an intensity below the $2.5\sigma(I)$ level were treated as unobserved. The structures were solved by means of the heavy-atom method. The Fe atoms of **3** were located by using an E^2 Patterson synthesis and those of **7** by using the symbolic addition program set SIMPEL.[8] The C, N, and O atomic positions of **3** were derived from a F_o-Fourier synthesis, and those of **7** from a ΔF-Fourier synthesis. The H atoms of **3** were excluded and those of **7** were located via a ΔF-Fourier synthesis after anisotropic refinement of the non-hydrogen atoms and were refined isotropically. The refinement of the non-hydrogen atoms proceeded by using anisotropic block-diagonal least-squares calculations. For **7** an empirical absorption correction (DIFABS)[9] was applied. The calculations were perfomred with XRAY76,[10] the atomic scattering factors were taken from Cromer and Mann,[11] and the dispersion correction factors were taken from ref 12.

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(7) The easy loss of one CO ligand from **10** is also seen in its FD mass spectrum where the highest mass observed corresponds to M^+ − CO (see Table I).

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

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

(10) Stewart, J. M. *The XRAY76 System*, Technical Report TR446; Computer Science Center, University of Maryland: College Park, MD, 1976.

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

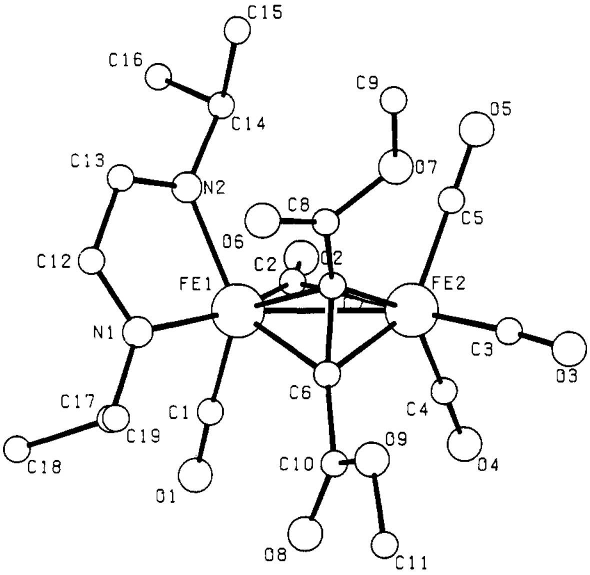

Figure 1. PLUTO drawing of $Fe_2(CO)_5(i\text{-Pr-DAB})[\mu_2,\eta^2\text{-MeOC(O)C}\equiv\text{CC(O)OMe}]$ (3).

Results and Discussion

$Fe_2(CO)_6(i\text{-Pr-DAB})$ (1) reacts with dimethyl acetylenedicarboxylate (DMADC) at 20 °C to give $Fe_2(CO)_5(i\text{-Pr-DAB})[\mu_2,\eta^2\text{-MeOC(O)C}\equiv\text{CC(O)OMe}]$ (3) in high yield.[6] The crystal structure of this complex, which contains a chelating α-diimine ligand and a perpendicular bridging alkyne molecule, has been determined.

Complex 3 reacts further in various different ways, depending on the reaction conditions and the other reactants present in solution (see Experimental Section).

Recently we reported the reactions of 3 with DMADC and methyl propynoate.[6] In the resulting products a second alkyne molecule is C–C coupled to the coordinated alkyne in 3 to form, with the Fe atom to which the DAB is coordinated, a ferracyclopentadienyl fragment in the compounds $Fe_2[\text{MeOC(O)C}{=}\text{CR}'\text{C(C(O)OMe}{=}\text{CC(O)OMe}](CO)_4(i\text{-Pr-DAB})$ (**4a**, R′ = C(O)OMe; **4b**, R′ = H) (see Scheme I).

Complex 3 reacts with CO to give $Fe_2(CO)_5[i\text{-PrN}{=}\text{CHCHN}(i\text{-Pr})\text{C(O)C(C(O)OMe)}{=}\text{CC(O)OMe}]$ (9), containing a flyover type ligand resulting from the coupling of one of the DAB N atoms and an alkyne molecule to a CO ligand (see Scheme I). This complex is isostructural to the recently reported complex $Fe_2(CO)_5[i\text{-PrN}{=}\text{CHCHN}(i\text{-Pr})\text{C(O)C(H)}{=}\text{CC(O)OMe}]$ which is formed in the reaction of 1 with methyl propynoate.[13] Complex 9 reacts with CO to give $Fe_2(CO)_6[i\text{-PrN}{=}\text{CHCHN}(i\text{-Pr})\text{C(O)C(C(O)OMe}{=}\text{CC(O)OMe}]$ (10), which is analogous to the reactions observed for the methyl propynoate derivatives.[13] This product (10) results from the addition of one CO ligand to the $Fe(CO)_2$ fragment in 9 with concomitant fission of the metal–metal bond. When a solution of 10 is purged with N_2, it easily loses one CO ligand and complex 9 is formed again in high yield.

Table VII. Selected Bond Lengths (Å) of Molecule 1 of 7 (Esd's in Parentheses)

Fe(1)–Fe(2)	2.583 (2)	C(9)–C(10)	1.469 (11)
Fe(1)–C(8)	2.011 (8)	C(12)–N(1)	1.512 (10)
Fe(1)–N(1)	1.973 (6)	C(15)–C(16)	1.395 (11)
Fe(1)–N(2)	1.996 (6)	C(15)–N(1)	1.360 (10)
Fe(2)–C(15)	2.046 (7)	C(16)–N(2)	1.456 (10)
Fe(2)–C(16)	2.109 (7)	C(17)–C(18)	1.491 (12)
Fe(2)–N(1)	2.036 (6)	C(17)–C(19)	1.494 (12)
C(7)–C(8)	1.480 (11)	C(17)–N(2)	1.312 (10)
C(8)–C(9)	1.308 (11)		

Table VIII. Selected Bond Angles (deg) of Molecule 1 of 7 (Esd's in Parentheses)

Fe(2)–Fe(1)–C(8)	147.7 (2)	Fe(2)–C(15)–N(1)	70.1 (6)
Fe(2)–Fe(1)–N(1)	51.0 (2)	C(16)–C(15)–N(1)	114.0 (8)
Fe(2)–Fe(1)–N(2)	73.8 (3)	Fe(2)–C(16)–C(15)	68.0 (6)
C(8)–Fe(1)–N(1)	99.7 (4)	Fe(2)–C(16)–N(2)	101.4 (6)
C(8)–Fe(1)–N(2)	91.7 (4)	C(15)–C(16)–N(2)	113.4 (8)
N(1)–Fe(1)–N(2)	83.6 (4)	C(18)–C(17)–C(19)	116.0 (10)
Fe(1)–Fe(2)–C(15)	72.8 (3)	C(18)–C(17)–N(2)	121.6 (8)
Fe(1)–Fe(2)–C(16)	70.5 (3)	C(19)–C(17)–N(2)	122.3 (9)
Fe(1)–Fe(2)–N(1)	48.8 (2)	Fe(1)–N(1)–Fe(2)	80.2 (4)
C(15)–Fe(2)–C(16)	39.2 (3)	Fe(1)–N(1)–C(12)	127.4 (5)
C(15)–Fe(2)–N(1)	38.9 (3)	Fe(1)–N(1)–C(15)	111.8 (6)
C(16)–Fe(2)–N(1)	67.7 (4)	Fe(2)–N(1)–C(12)	126.3 (5)
Fe(1)–C(8)–C(7)	114.3 (6)	Fe(2)–N(1)–C(15)	70.9 (6)
Fe(1)–C(8)–C(9)	124.2 (7)	C(12)–N(1)–C(15)	119.4 (7)
C(7)–C(8)–C(9)	121.5 (8)	Fe(1)–N(2)–C(16)	103.7 (6)
C(8)–C(9)–C(10)	124.8 (9)	Fe(1)–N(2)–C(17)	135.1 (6)
Fe(2)–C(15)–C(16)	72.9 (7)	C(16)–N(2)–C(17)	121.0 (8)

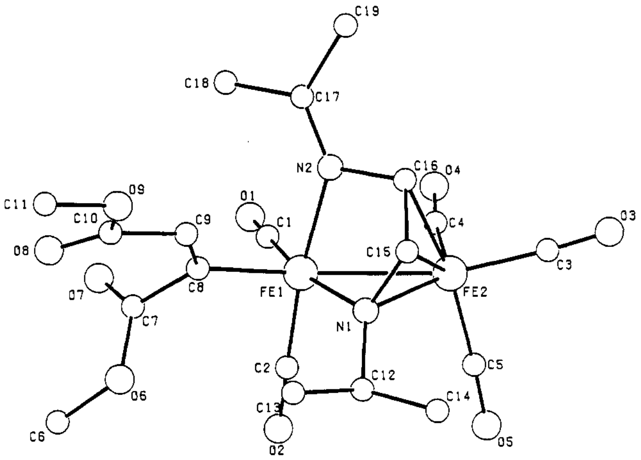

Figure 2. PLUTO drawing of molecule 1 of $Fe_2(CO)_5[Me_2C{=}\text{NCHCHN}(i\text{-Pr})][\eta^1\text{-MeOC(O)C}{=}\text{CHC(O)OMe}]$ (7).

Finally, complex 3 at 60 °C undergoes a thermally induced isomerization, which involves an unusual alkyl C–H activation. The methine proton of one of the DAB isopropyl groups is transferred to one of the alkyne C atoms of the coordinated DMADC. In this reaction two different isomers are formed (6 and 7). Of one of these complexes, $Fe_2(CO)_5[Me_2C{=}\text{NCHCHN}(i\text{-Pr})][\eta^1\text{-MeOC(O)C}{=}\text{CHC(O)OMe}]$ (7), the X-ray crystal structure has been determined (see Figure 2 and Tables VII and VIII).

Molecular Structures of 3 and 7. The molecular structure of 3 (see Figure 1) consists of an $Fe(CO)_3$ unit and an $Fe(CO)(\sigma,\sigma\text{-}N,N'\text{-}i\text{-Pr-DAB})$ fragment linked by a formally single Fe–Fe bond [Fe(1)–Fe(2) = 2.5628 (16) Å]. Further, both Fe centers are bridged by a semibridging CO ligand [Fe(1)–C(2) = 1.804 (8) Å; Fe(2)–C(2) = 2.337 (8) Å][14] and a DMADC molecule in the μ_2,η^2-perpendicular bridging coordination mode. The alkyne–Fe bond distances [Fe(1)–C(6) = 1.974 (7) Å; Fe(1)–C(7) = 2.019 (7) Å; Fe(2)–C(6) = 1.960 (7) Å; Fe(2)–C(7) = 1.944 (7) Å] show that the alkyne is slightly closer to Fe(2) and twisted from the ideal perpendicular position. This deviation is most likely due to steric interactions of the alkyne R groups with the diimine ligand. The C(6)–C(7) distance of 1.344 (10) Å is normal for an alkyne molecule in this coordination

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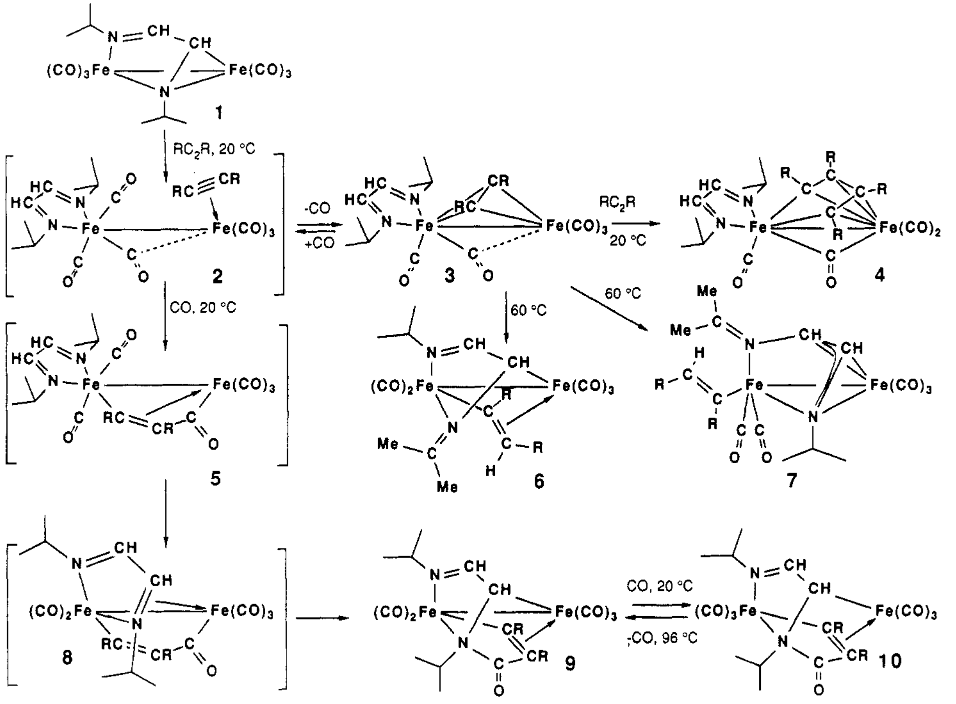
(12) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV.

(13) Part 2 of this series: Muller, F.; van Koten, G.; Vrieze, K.; Heijdenrijk, D. *Organometallics* **1989**, *8*, 33.

(14) Colton, R.; McCormick, M. J. *Coord. Chem. Rev.* **1980**, *31*, 1.

Scheme I. Reactions of $Fe_2(CO)_6$(*i*-Pr-DAB) and Dimethyl Acetylenedicarboxylate (R = *i*-Pr, R′ = C(O)OMe; 4a, R″ = H; 4b, R″ = C(O)OMe)[a]



[a] Compounds between brackets are proposed intermediates.

mode.[15] This also applies for the C(6)–C(7)–C(8) and C(7)–C(6)–C(10) angles of 142.3 (8) and 140.2 (7)°, respectively. Fullfilment of the 18e rule for both Fe centers would require a bridging CO ligand. The hard N-donor atoms of the DAB ligand, when compared to two terminal CO ligands, however, cause a relative excess of electron density on Fe(1).[16] This results in a shortening of the Fe(1)–C(2) distance and an larger Fe(1)–C(2)–O(2) angle which enables Fe(1) to be relieved of this excess of electron density through better orbital overlap and consequently a stronger π-back-bonding.

In the molecular structure of 7 (see Figure 3) the asymmetric unit contains two independent, but virtually identical molecules. Only one of these molecules will be discussed. The molecule has a number of interesting features when compared to its isomer 3. First, the 4e donating chelating DAB ligand in 3 is transformed into a formally 7e donating bridging σ,σ,*N*,*N*′-(1-dimethylketimino)-*N*-isopropyl-3-azaallyl ligand. The N(1)–C(15) and C(15)–C(16) distances within the azaallyl ligand of 1.360 (10) and 1.395 (11) Å, respectively, and the distances from this ligand to Fe(2) [Fe(2)–N(1) = 2.036 (6), Fe(2)–C(15) = 2.046 (7), and Fe(2)–C(16) = 2.109 (7) Å] are in the range observed for previously reported azaallyl metal carbonyl complexes.[17] The transformation of one of the N-*i*-Pr fragments of the DAB into a dimethylketimino fragment, which is σ-N coordinated as a 2e donor to Fe(1), is very unusual. The imine nature of this fragment is shown by the N(2)–C(17) distance of 1.312 (10) Å and the trigonal bond angles around C(17). The N atom of the azaallyl moiety is also bonded as a σ-N 2e donor to Fe(1), while the azaallyl ligand donates three electrons to Fe(2) when regarded as a neutral ligand. The μ_2,η^2-bridging DMADC ligand is transformed into an η^1-(*cis*-1,2-bis(methoxycarbonyl))vinyl ligand [C(8)–C(9) = 1.308 (11) Å] bonded to Fe(1), to which also both N atoms are coordinated, via the addition of the former *i*-Pr methine proton to one of the alkyne C atoms. Both Fe centers are linked by a formally single Fe–Fe bond [Fe(1)–Fe(2) = 2.583 (2) Å]. Finally, it is worthy noting that the molecular structure of 7 is reminiscent of that of $Ru_2(CO)_5[RNCHCHN(R)C(O)CH_2CH_2]$ (11) which is formed when a solution of $Ru_2(CO)_6$(R-DAB) [R = *i*-Pr, *c*-Hex] (isostructural with 1) is treated at room temperature with ketene ($H_2C{=}C{=}O$).[4g] The structure is also similar to that of $Fe_2(CO)_5[RNCHCHN(R)C(O)C(Me){=}CNEt_2]$ (12) which is formed in the reaction of 1 with $MeC{\equiv}CNEt_2$.[18]

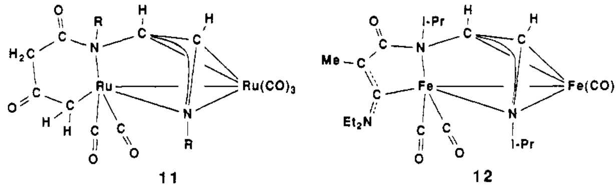


Figure 3. Schematic representation of compounds 11 and 12.

NMR Spectroscopy. The ^1H and ^{13}C NMR data of the reported compounds are listed in Tables II and III, respectively. The ^1H NMR of 3 shows the expected resonances for a σ,σ-N,N′ chelating DAB ligand[3] and two resonances for the OMe groups of the coordinated alkyne. The C atoms of the alkyne appear at 74.3 and 86.5 ppm. Variable-temperature NMR experiments indicate that complex 3 is fluxional in solution. Below 281 K the imine protons appear as two singlets, which at this temperature

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[15] Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858.

[16] Bertoncello, R.; Casarin, M.; Dal Colle, M.; Granozzi, G.; Mattogno, L.; Muller, F.; Russo, U.; Vrieze, K., manuscript in preparation.

[17] (a) Muller, F.; van Koten, G.; Vreize, K.; Krijnen, L. B.; Stam, C. H. *J. Chem. Soc., Chem. Commun.* **1986**, 150. (b) Keijsper, J.; Mul, J.; van Koten, G.; Vrieze, K.; Ubbels, H.; Stam, C. H. *Organometallics* **1984**, *3*, 1732. (c) Nakamura, Y.; Backmann, K.; Heimgartner, H.; Schmid, H. *Helv. Chim. Acta* **1978**, *61*, 589. (d) Polm, L. H.; Elsevier, C. J.; Vrieze, K. *Polyhedron*, in press.

[18] Part 8 of this series: Muller, F.; van Koten, G.; Kraakman, M. J. A.; Vrieze, K.; Heijdenrijk, D.; Zoutberg, M. C. *Organometallics*, following paper in this issue.

coalesce to a sharp singlet. The septets due to the *i*-Pr methine protons coalesce at about 306 K to give a broad signal. The two OMe singlets coalesce at 295 K and at higher temperatures sharpen to give a broad singlet. In the ^{13}C NMR spectrum of **3** at low temperatures (<245 K) the C atoms of the CO ligands appear as four signals: at 233.5 ppm [the semibridging C(2)O(2)], 214.2 ppm [C(1)O(1)], and two at 209.5 and 206.3 ppm, with relative intensities 2:1. The latter two signals broaden above 245 K and appear at 260 K as one broad signal at 208.8 ppm. The signals at 214.2 and 233.5 ppm remain unchanged at higher temperatures, apart from some decrease in intensity due to slower relaxation. This indicates that the C(1)O(1) and C(2)O(2) groups do not exchange. From these observations we conclude that two dynamic processes are involved. The first is the scrambling of the CO ligands on the $Fe(2)(CO)_3$ fragment and the second is the site exchange of the two σ-N atoms on Fe(1), which makes both halves of the DAB ligand and of the coordinated alkyne equivalent. We are, however, not able to derive from the present data via which mechanism this latter exchange reaction proceeds. The coalescence temperatures of 306 and 281 K for the methine and imine protons, respectively, suggest an activation energy for the latter fluxional process of 62 (±1) kJ·mol^{-1}. The process of scrambling the CO ligands on Fe(2) has an activation energy of 51 (±1) kJ·mol^{-1}.

The NMR data for **9** and **10** are similar to those of the earlier reported compounds $Fe_2(CO)_n$[RN=CHCHN(R)-C(O)CH=CC(O)OMe] (n = 5, 6; R = *i*-Pr, c-Hex), formed in the reaction of $Fe_2(CO)_6$(R-DAB) with methyl propynoate.[13] This is consistent with our conclusion that **9** and **10** are structurally analogous to these earlier complexes.

The NMR data of **7** in solution are in agreement with its solid-state molecular structure. The former imine protons resonate at 4.50 and 6.73 ppm, which is in agreement with the azaallylic character of the ligand.[17] The ^{13}C resonances at 71.5 and 123.4 ppm are also characteristic azaallyl C atoms. The migrated proton on the η^1-vinyl fragment resonates as expected in the olefinic region at 5.17 ppm. As a consequence of the H migration, the Me groups of the *i*-Pr moiety from which the methine proton has been abstracted no longer appear as two doublets but as two singlets, which are found at about 0.5 ppm upfield with respect to characteristic *i*-Pr Me resonance frequencies. The vinyl C atoms are found at 171.0 and 99.6 ppm, respectively.

In the ^1H NMR spectrum of **6** the proton that has migrated from an *i*-Pr group to the alkyne resonates at 6.10 ppm, which is a normal value for a proton on a μ_2,η^2-vinyl fragment.[19] The protons on the central C atoms of the former DAB skeleton resonate at 7.97 and 3.62 ppm, respectively. This indicates that one of the imine functions is fully retained, while the other imine C atom is σ-bonded to an Fe center. We therefore conclude that the intact imine moiety of the DAB skeleton is σ-N coordinated and the other N-*i*-Pr group is transformed into a $N{=}CMe_2$ fragment, which is also σ-N coordinated to the same Fe center. The alkyne is reduced to a μ_2,η^2-vinyl fragment, σ-bonded to that Fe center to which both N atoms are bonded and η^2-coordinated to the other one. The ^{13}C NMR resonances of the former DAB imine C atoms at 169.9 and 73.2 ppm, respectively, are supportive of this proposed structure (see Scheme I). The σ-bonded vinyl C atom resonates at 101.2 ppm, while the second vinyl C atom is found at 125.4 ppm.

Complex Formation. The first product that can be isolated from the reaction of $Fe_2(CO)_6$(*i*-Pr-DAB) (**1**) with DMADC at 20 °C is **3**. The coordination mode of the DAB ligand has changed from the 6e donating σ-N,μ_2-N′,η^2-C=N′ bridging bonding mode to the chelating 4e donating σ,σ-N,N′ bonding mode. The alkyne is in the μ_2,η^2-perpendicular bridging bonding mode, donating two electrons to each Fe center. No intermediate complex between **1** and **3** could be isolated or observed spectroscopically. In the proposed reaction mechanism, however, the first step is substitution of the η^2-C=N coordinated imine fragment of the DAB ligand by an η^2-C≡C coordinated alkyne, to give intermediate **2** (see Scheme I). Complex **3** is subsequently formed through the substitution of one of the CO ligands on the Fe(DAB) fragment by the second η^2-C≡C coordination of the alkyne. Although many dinuclear complexes with perpendicular bridging alkynes are known,[15] relatively few of these are Fe complexes. One of the first examples was $Fe_2(CO)_6$(*t*-BuC≡CH) which, however, contains a formally double Fe=Fe bond of 2.316 (1) Å.[20]

The formation of the ferracyclopentadienyl complexes **4** has already been subject to another paper in this series.[6] Until now in the formation of these ferracyclopentadienyl complexes no intermediates with two uncoupled coordinated alkyne molecules have been found. A likely route for the formation of the ferracycle in **4** is a direct attack of the second alkyne to the coordinated alkyne and the $Fe(CO)_3$ fragment in **3**, as was described by Hoffmann et al.[21]

The formation of the flyover complex **9** proceeds by a more complex mechanism. This type of complexes has been the subject of a previous publication,[13] concerning the formation of structurally analogous flyover complexes in the reaction of $Fe_2(CO)_6$(R-DAB) with methyl propynoate. We propose that the presently reported complexes **9** and **10** are formed in a similar fashion (see Scheme I). This mechanism involves the conversion of **2** to **5** via the attack of the η^2-coordinated alkyne in **2** on one of the CO ligands. Complex **5** is then converted, via the substitution of the η^2-C=C bonded olefinic fragment by a C=N moiety which becomes η^2-C=N coordinated, to give intermediate **8**. The bridging N atom of the coordinated imine fragment is subsequently N–C coupled to the ketonic C atom, resulting in the flyover complex **9** This latter complex reacts with CO to give **10**, via the addition of a CO group to the $Fe(CO)_2$ fragment and concomitant fission of the Fe–Fe bond.

The important difference between the reactions of **1** with methyl propynoate and dimethyl acetylenedicarboxylate is that in the case of the latter substrate the formation of **9** only proceeds in the presence of CO. When no CO is present, the elimination of one CO ligand from **2** to give **3** is preferred over C–C bond formation to give **5**. In the presence of CO, the μ_2,η^2-coordinated alkyne in complex **3** is transformed into a monodentate ligand in **2**, and the reaction can proceed via **5** to give the thermodynamically most stable products **9** and **10**.

The thermally induced isomerization of **3** into **6** and **7** is no doubt the most unusual reaction reported here. Because no intermediate compounds could be observed or isolated in this conversion, it is difficult be certain about the reaction mechanisms. The possibility of the initial hydrogen transfer from an isopropyl group to one of the metal centers to form an hydride intermediate does not

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

[20] Cotton, F. A.; Jamerson, J. D.; Stults, B. R. *J. Am. Chem. Soc.* **1976**, *98*(7) 1774.

[21] Thorn, D. L.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*(1), 126.

seem very likely because of the large distance between the methine protons and the Fe centers in **3**. A direct intramolecular proton transfer from a methine C atom to one of the alkyne C atoms seems more likely. This is supported by the molecular structure of **3** where the distance of the calculated position of the proton on C(14) and the alkyne C atom C(7) is 3.54 Å. For the proton on C(17) and the alkyne C(6) atom this distance is 2.85 Å. It seems likely that these relatively short distances, together with the fluxional movement of the ligand **3** in solution, facilitate the hydrogen transfer process. A comparable reaction that involves a direct H transfer from an η^5-C_5H_5 ligand to an η^2-alkyne coordinated to the same Fe center in CpFe(CO)(PPh_3)(MeC≡C(O)OEt), to give an η^1-vinyl fragment, has been reported by Reger at al.[22] The formation of two different isomers **6** and **7** probably results from comparable reactivity of both *i*-Pr methine groups in **3**. Hydrogen abstraction from the isopropyl group on N(1), in the Fe(1)–Fe(2)–C(2) plane, leads to the formation of **7** with a terminal $Me_2C{=}N$ group. Migration of the methine proton from the isopropyl group on N(2) to the alkyne results in a bridging $N{=}CMe_2$ group, as is observed in **6**. The difference in the above-mentioned H(14)–C(7) and H(17)–C(6) distances may explain the 1:2 ratio of the yields of **6** and **7**.

In contrast to the reactions of coordinated α-diimine ligands involving reactions of the C=N bond(s), such as C—C and C—N coupling reactions and hydrogenation reactions,[4] those involving the aliphatic substituents of the ligands have few precedents. To our knowledge they are limited to two examples. The first is the metalation of a diisopropylmethyl substituent on the DAB ligand in $NiBr_2$(*N*,*N*′-bis(diisopropyl)methyl-DAB), when it is reacted with *o*-tolylmagnesium bromide.[23] The second example is the metalation of the methyl group on the pyridyl fragment in $Os_3(CO)_9$(6-methylpyridine-2-(*N*-isopropyl)carbaldimine).[24]

Conclusions

It has become clear that the initial step in the reaction of $Fe_2(CO)_6$(R-DAB) with DMADC involves the substitution of the η^2-C=C bonded imine moiety by an alkyne molecule. The resulting intermediate **2** has as yet never been isolated or observed but nevertheless seems to be a likely key intermediate in the formation of various reaction products.

From classical metal carbonyl/alkyne chemistry it is already known that alkynes that are coordinated to more than one metal center may react further in many different ways.[25] The results reported here show that the ability of the α-diimine ligand to participate in N–C coupling reactions and hydrogen transfer processes may greatly extend this versatile reactivity.

The formation of products of hydrogen migration demonstrates that the reactivity of coordinated α-diimine ligands is not limited to C—C and C—N coupling and hydrogenation reactions involving the N=C fragments but that the aliphatic substituents may also participate in the conversions.

The initial formation of **3** via **2**, and the subsequent reverse reaction of **3** with CO, via **2**, **5**, and **8**, to give the flyover complex **9** clearly shows that the product distribution in the presently discussed reactions is governed by subtle differences in the relative thermodynamic and kinetic stabilities of the intermediates and isolated complexes. The fact that **3** reacts with CO to give the flyover complexes **9** and **10** also provides us with important information about the formation of similar flyover complexes in the reaction of **1** with methyl propynoate.[18]

Finally, we can conclude that the reactivity of **1** toward dimethyl acetylenedicarboxylate is comparable to the reactivity of **1** toward methyl propynoate as far as the formation of ferracyclopentadienyl of flyover complexes is concerned. Their reactivities differ significantly, however, with respect to the hydrogen migration processes, which only occur in case of the DMADC complex **3**. This, taken together with the fact that in the reaction of **1** with MP no complex like **3** is found, confirms that the thermodynamic stability of the reaction products is governed by small differences in steric and electronic properties of the metals, ligand, and alkyne used.

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Supplementary Material Available: Tables of fractional coordinates and the anisotropic thermal parameters of the nonhydrogen atoms, full listings of bond lengths and angles of the non-hydrogen atoms, and stereoscopic ORTEP representations for **3** and **7** and a table of fractional coordinates and isotropic thermal parameters of the hydrogen atoms and a listing of bond lengths and angles of the hydrogen atoms for **7** (13 pages); listings of observed and calculated structure factors for **3** and **7** (31 pages). Ordering information is given on any current masthead page.

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