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Reversible C–C Coupling Reactions Between Alkynes and CO Ligands on Di-iron α-Diimine Complexes*

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Abstract

$Fe_2CO)_6(L)$ [L = i-Pr-DAB, i-Pr-Pyca] (**1**) and $Fe_2(CO)_7(2,2'\text{-bipyridine})$ (**2**) react with RC≡CC(O)OMe [R = H, C(O)OMe] to give the complexes $Fe_2[\mu_2\text{-}R'C{=}C(R'')C(O)](CO)_5(\sigma,\sigma\text{-}N,N'\text{-}L)$ [L = i-Pr-DAB: R′ = H, R″ = C(O)OMe (**5a**); L = i-Pr-Pyca: R′ = H, R″ = C(O)OMe (**5b**); R′ = C(O)OMe, R″ = H (**5c**); R′ = R″ = C(O)OMe (**5d**); L = 2,2′-bipyridine (bipy): R′ = R″ = C(O)OMe (**5e**)] in yields varying from <5% for L = i-Pr-DAB to almost quantitative for L = bipy. The X-ray single crystal structure of $Fe_2[\mu_2\text{-}MeOC(O)C{=}CH\text{–}C(O)](CO)_5(\text{i-Pr-Pyca})$ (**5c**) has been determined.

The purple crystals of $Fe_2C_{19}H_{16}N_2O_8$, M = 512.04, are triclinic, space group $P\bar{1}$, a = 10.1428(11), b = 10.7084(16), c = 10.0367(10) Å, α = 94.368(9)°, β = 100.927(13)°, γ = 93.552(13)°, Z = 2. A total of 2507 absorption corrected reflections (Cu Kα, μ = 114.18 cm^{-1}) have been used in the refinement resulting in a final R value of 0.036 (R_w = 0.054).

The molecular structure of **5c** consists of an $Fe(CO)_3$ and an $Fe(CO)_2(\sigma,\sigma\text{-}N,N'\text{-i-Pr-Pyca})$ unit linked by a single Fe–Fe bond [Fe(1)–Fe(2): 2.7191(9) Å], that is bridged by an organic MeOC(O)C=C(H)–C(O) fragment, resulting from the C–C coupling of a CO ligand and a methyl propynoate molecule. This fragment is σ-bonded via the C(C(O)OMe) atom to the $Fe(CO)_2(Pyca)$ center and via the C(O) atom to the $Fe(CO)_3$ center to which also the olefinic bond is π-coordinated.

The complexes **5**, which are most likely formed via an intermediate with a chelating α-diimine and an η^2-C≡C bonded alkyne, react with a second equivalent of alkyne to give the ferracyclopentadienyl complexes $Fe_2[RC{=}CR\text{–}CR{=}CR](CO)_4(L)$. These reactions probably proceed via the fission of the C–C bond between the CO and the alkyne in **5**, followed by the loss of a CO ligand. The resulting intermediate with the alkyne in the μ_2,η^2-perpendicular bonding mode reacts with the second alkyne molecule. Heating of **5b, c** yields the ferracyclopentadienyl complexes $Fe_2[MeOC(O)C{=}CHC(C(O)OMe){=}CH](CO)_4\text{-}(\text{i-Pr-Pyca}(\mathbf{4e}))$. When R′ = R″ = C(O)OMe ferracyclopentadienyl complexes are formed with the α-diimine bonded to the Fe in the ferracycle, whereas in the case of R′ = H/C(O)OMe and R″ = C(O)OMe/H the formation of ferracyclopentadienyl complexes with the α-diimine bonded to the second Fe center is observed. This product distribution is probably the result of the steric properties of the alkynes.

Introduction

α-Diimine ligands coordinated to metal carbonyl complexes are known to exhibit a versatile coordination behaviour, that is originating from their ability to donate from 2 up to 8 electrons to the metal(s) to which they are bonded via the lone pairs on the N atoms and the π-electrons of the C=N bonds. The resulting α-diimine complexes have shown an extensive reactivity towards a range of substrates, involving C–C, C–N, C–H and N–H coupling reactions [2].

$Ru_2(CO)_6(\text{R-DAB})$, in which the R-DAB [R-DAB = 1,4-diaza-1,3-butadiene: RN=CHCH=NR] is coordinated as a σ-N,μ_2-N′,η^2-C=N′ 6e donor, reacts with alkynes, to a number of interesting organometallic compounds which all result from the initial C–C coupling of the alkyne to the η^2-C=N coordinate imine C atom [3]. These observations prompted us to carry out a systematic study of the reactivity of alkynes towards $M_2(CO)_6(L)$ complexes in which M_2 is not only Ru_2, but can also be Fe_2 or FeRu and L = R-DAB or R-Pyca (2-pyridine-carbaldimine: $C_5H_4N\text{-}2\text{-}C(H){=}NR$).

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*Reactions of Dinuclear Metal Carbonyl α-Diimine Complexes with Alkynes, Part 5. For Part 4 see ref. 1.

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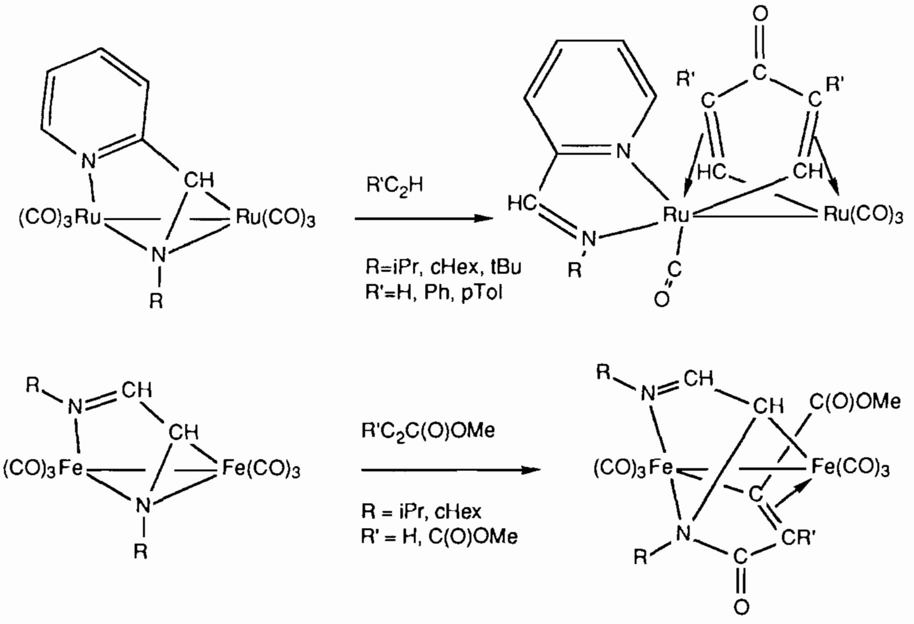

Scheme 1. Formation of flyover type ligands in reactions of $Fe_2(CO)_6$(R-DAB) and $Ru_2(CO)_6$(R-Pyca) with alkynes.

Furthermore we found that $Ru_2(CO)_6$(R-Pyca) [R = i-Pr, c-Hex, t-Bu], which is isostructural with $Ru_2(CO)_6$(R-DAB), reacts thermally with R'C≡CH [R' = *p*-Tol, Ph, H] to give the complexes Ru_2[HC=C(R')C(O)C(R')=CH]$(CO)_4$(R-Pyca) [4a] in which two alkynes are C–C coupled to a CO molecule resulting in a bridging organic ligand of the well-known flyover type, as in Fe_2[MeC=CMeC(O)-CMe=CMe]$(CO)_6$ (see Scheme 1) [4b]. Moreover we have found that $Fe_2(CO)_6$(R-DAB) (**1a**) reacts with MeOC(O)C≡CR' [R' = H, C(O)OMe)] at room temperature to give the complexes $Fe_2(CO)_5$[RN=C(H)C(H)N(R)C(O)C(R')=CC(O)OMe] (**9**) containing an organic ligand that is isostructural to the above-mentioned flyover ligands, but with an imine fragment, instead of one of the alkynes, coupled to the CO group (see Scheme 1) [5, 6]. In both reactions no intermediate complexes could be isolated or observed, which made the formulation of a mechanism for the formation of these complexes impossible.

$Fe_2(CO)_6$(i-Pr-Pyca) (**1b**) [7] however, reacted with methyl propynoate to give Fe_2[μ_2-MeOC(O)C=C(H)C(O)]$(CO)_5$(i-Pr-Pyca) (**5c**), of which the structure was confirmed by an X-ray crystal structure determination. This complex contains a bridging RC=C(H)C(O) fragment resulting from the C–C coupling of an alkyne to a CO. This type of bridging ligands is generally regarded to play an important role in the formation of flyover ligands [8].

We therefore were interested in whether this compound and a number of related complexes could react further to give one of the above-mentioned flyover type complexes. We now report the preparation, characterization and reactivity of the complexes Fe_2[μ_2-alkyne-CO]$(CO)_5$(L) (**5**) [L = i-Pr-DAB, i-Pr-Pyca, 2,2'-bipyridine; alkyne = mp, dmadc] as well as the X-ray crystal structure of Fe_2[μ_2-MeOC(O)C=CH–C(O)]$(CO)_5$(i-Pr-Pyca) (**5c**).

Experimental

Materials and Apparatus

^1H and ^{13}C NMR spectra were recorded on a Bruker AC100 spectrometer. 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. Column chromatography was performed using silica-gel (60 Mesh, dried and activated before use) as the stationary phase. $Fe_2(CO)_6$(i-Pr-DAB) [9], $Fe_2CO)_6$-(i-Pr-Pyca) [7] and $Fe_2(CO)_7$(2,2'-bipyridine) [10] were prepared according to known procedures. Methyl propynoate (MP) and dimethyl acetylene-dicarboxylate (DMADC) were used as commercially obtained.

TABLE 1. FD-mass, IR and Analytical Data of 5a–e, 7b, c, c′

	FD-mass[a] obs. (calc.)	IR (ν_sC=O) (cm^{-1}, CH_2Cl_2)	Elemental analysis: obs. (calc.) (%)		
			C	H	N
5a	504 (504.06)	2027(s), 1991(vs), 1956(s), 1930(sh), 1761(s), 1708(s)	not analyzed		
5b	511 (512.04)	2031(s), 1995(vs), 1970(s), 1949(s), 1758(s), 1706(s)	43.39 (44.57)	3.19 (3.15)	5.24[b] (5.47)
5c	511 (512.04)	2031(s), 1995(vs), 1970(s), 1949(s), 1758(s), 1706(s)	43.39 (44.57)	3.19 (3.15)	5.24[b] (5.47)
5d	570 (570.07)	2042(s), 1998(vs), 1985(sh), 1954(s), 1744(s), 1711(s)	41.15 (44.25)	3.33 (3.18)	4.38 (4.91)
5e	not measured	2034(s), 1993(vs), 1976(s), 1944(s), 1748(m), 1718(s)[c]	45.63 (45.71)	2.65 (2.44)	4.05 (4.85)
7b	664 (664.14)	2029(s), 1977(s,b), 1824(m), 1722(m), 1687(m)	47.48 (47.02)	3.52 (3.04)	4.05 (4.22)
7c	606 (606.11)	2048(s), 1972(s,b), 1823(m), 1713(m), 1682(m)	not analyzed		
7c′	606 (606.11)	2021(s), 1972(s,b), 1823(m), 1713(m), 1682(m)	not analyzed		

[a] Based on ^{57}Fe. [b] Analysis of an inseparable mixture of the isomeric 5b and 5c. [c] In tetrahydrofuran solution.

The obtained products were identified by IR and mass spectroscopy and elemental analysis (Table 1) and by ^{1}H and ^{13}C NMR (Tables 2 and 3, respectively).

Synthesis of $Fe_2[\mu_2$-HC=C(C(O)OMe)C(O)]$(CO)_5$(i-Pr-DAB) (5a)

$Fe_2(CO)_6$(i-Pr-DAB) (**1a**) (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 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). 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-Pr-N=C(H)C(H)N(i-Pr)C(O)-C(H)=CC(O)OMe} [**9a**: n = 5, **10a**: n = 6] [6]. Further elution with hexane/diethyl ether (1:1) and hexane/diethyl ether (1:3) produced the yellow complex $Fe_2(CO)_6$[i-PrNC(H)C(H)N(i-Pr)C(H)CC(O)-OMe] [11] in an average yield of 30% based on 1. The subsequent fraction produced in low yield (<5%) the blue complex $Fe_2[\mu_2$-HC=C(C(O)OMe)-C(O)]$(CO)_5$(i-Pr-DAB) (5a).

TABLE 2. ^{1}H NMR Data of 5a–e, 7b, c, c′ [a]

5a	1.53 (12H, d, 6 Hz: i-Pr Me); 3.76 (3H, s: OMe) 4.87, 5.26 (1H, sept, 6 Hz: i-Pr CH); 8.02, 8.31 (1H, s: N=CH); 9.55 (1H, s: C=CH)
5b	1.62 (6H, d, 6 Hz: i-Pr Me); 3.74 (3H, s: OMe); 4.66 (1H, sept, 6 Hz: i-Pr CH); 7–8 (4H, m: pyr); 8.60 (1H, s: N=CH); 9.48 (1H, s: C=CH)
5c	1.56 (6H, d, 6 Hz: i-Pr Me); 3.91 (3H, s: OMe); 4.24 (1H, s: C=CH); 4.60 (1H, sept, 6 Hz: i-Pr CH); 7–9 (4H, m: pyr); 8.53 (1H, s: N=CH)
5d	1.55/1.63 (6H, dd, 6 Hz: i-Pr Me); 3.73, 3.98 (3H, s: OMe); 4.63 (1H, sept, 6 Hz: i-Pr CH); 7–8 (3H, m: py); 8.28 (1H, d, 6 Hz: py H6); 8.53 (1H, s: N=CH)
5e	3.70, 3.99 (6H, s, s: OMe); 7.2–8.1 (6H, m: bipy); 8.37, 9.07 (2H, d, d, 6 Hz: bipy)
7b	2.75, 3.67, 3.68, 3.84 (12H, 4xs: OMe); 7–8 (6H, m: bipy); 8.71, 9.11 (2H, d, d, 6 Hz: bipy)
7c	3.32, 3.07, 3.77 (9H, 3xs: OMe); 6.64 (1H, s, CH); 7–8 (6H, m: bipy); 8.85, 9.36 (2H, d, d, 6 Hz: bipy)
7c′	2.80, 3.70, 3.73 (9H, 3xs: OMe); 7.22 (1H, s, CH); 7–8 (6H, m: bipy); 8.51, 9.08 (2H, d, d, 6 Hz: bipy)

[a] Measured in $CDCl_3$ solution, 20 °C, spectrometer frequency 100 MHz, chemical shift values in ppm relative to Me_4Si. The H^3, H^4 and H^5 resonances of the pyridyl fragments are generally not resolved.

Synthesis of $Fe_2[\mu_2$-RC=CR′C(O)]$(CO)_5$(i-Pr-Pyca) [5b: R = H, R′ = C(O)OMe; 5c: R = C(O)OMe, R′ = H]

$Fe_2(CO)_6$(i-Pr-Pyca) (**1b**) (1 mmol, 428 mg) and methyl propynoate (3 mmol, 252 mg) were stirred in 50 ml of hexane at 40 °C. After 26 h the dark precipitate was collected on a sintered glass filter and washed with 20 ml of hexane, solved in CH_2Cl_2 and purified by column chromatography. Elution with hexane/diethyl ether (2:3) produced a minor amount of Fe_2[MeOC(O)C=C(H)C(H)=CC(O)OMe]$(CO)_4$(i-

TABLE 3. ^{13}C NMR Data of 5b–e, 7b^{a}

5b^{b}	23.0, 25.3 (i-Pr Me); 48.1 (C^2); 52.6 (OMe); 64.7 (i-Pr CH); 125.3 (py C^5); 127.3 (py C^4); 137.0 (py C^3); 152.0 (py C^6); 154.4 (py C^2); 158.4 (N=CH); 163.1 (C^1); 169.1 (OC=O); 209.9, 213.4 (COs); 233.0 (C^3)
5c^{b}	22.3, 25.8 (i-Pr Me); 44.2 (C^2); 52.9 (OMe); 63.7 (i-Pr CH); 124.9 (py C^5); 127.7 (py C^4); 136.7 (py C^3); 152.5 (py C^6); 153.9 (py C^2); 158.3 (N=CH); 159.6 (C^1); 176.8 (OC=O); 201.6, 211.6, 214.3 (COs); 233.3 (C^3)
5d^{c}	22.5, 25.8 (i-Pr Me); 50.4 (C^2); 52.7 (OMe); 64.3 (i-Pr CH); 125.6 (py C^5); 127.4 (py C^4); 137.0 (py C^3); 152.6 (py C^6); 153.7 (py C^2); 158.3 (N=CH); 167.4 (C^1); 176.1 (OC=O); 209.9 (COs); 234.1 (C^3)
5e^{b}	52.8, 53.9 (OMe); 49.3 (C^2); 122.4, 123.1, 126.1, 126.6, 137.3, 137.8, 139.3, 139.5 (bipyridine); 153.8, 155.5 (bipyridine C^2); 167.6 (C^1); 176.4, 179.8 (OC=O); 210.9, 211.5 (COs); 237.1 (C^3)
7b^{d}	50.8, 51.9, 52.8, 53.1 (OMe); 115.5, 122.9 (C=c–c=C); 121.1, 121.2, 121.5, 123.9, 125.9, 126.2, 136.9, 137.1 (bipyridine); 156.0, 156.4 (bipyridine C^2); 163.2, 166.9 (c=C–C=c); 165.1, 165.5, 172.6, 176.8 (OC=O)

^{a}Measured in $CDCl_3$ solution, spectrometer frequency 25 MHz, chemical shift values in ppm relative to Me_4Si. C^1, C^2, C^3 correspond with $Fe{-}C^1{=}C^2{-}C^3({=}O){-}Fe$. ^{b}Measured at 0 °C. ^{c}Measured at 5 °C. ^{d}Measured at 20 °C.

Pr-Pyca) (**6a**)*. A mixture of **5b** and **5c** in an about 1:2 ratio was obtained by elution with hexane/diethyl ether (1:4) with a total yield of about 50%. Dark purple crystals of **5b** and **5c** were obtained by recrystallization from hexane/diethyl ether (3:2) at −80 °C.

Synthesis of $Fe_2[\mu_2\text{-}MeOC(O)C{=}C(C(O)OMe)C(O)](CO)_5(i\text{-}Pr\text{-}Pyca)$ (5d)

$Fe_2(CO)_6$(i-Pr-Pyca) (**1b**) (1 mmol, 428 mg) and dimethyl acetylenedicarboxylate (3 mmol, 426 mg) were stirred in hexane for 28 h at 20 °C. The reaction mixture was evaporated to dryness and separated by column chromatography. The first fraction (diethyl ether/CH_2Cl_2 (9:1)) yielded the dark purple complex $Fe_2[\mu_2\text{-}MeOC(O)C{=}C(C(O)OMe)C(O)](CO)_5$(i-Pr-Pyca) (**5d**) in 60–70% yield. Elution with diethyl ether/CH_2Cl_2 (3:2) produced a second fraction containing a 1:2 mixture of two isomeric ferracyclopentadienyl complexes $Fe_2[MeOC(O)C{=}C(C(O)OMe)C(C(O)OMe){=}CC(O)OMe](CO)_4$(i-Pr-Pyca) (**7a** and **7a′**)* in yields varying from 10–20%.

Synthesis of $Fe_2[\mu_2\text{-}MeOC(O)C{=}C(C(O)OMe)C(O)](CO)_5$(2,2′-bipyridine) (5e)

$Fe_2(CO)_7$(2,2′-bipyridine) (**2**) (1 mmol, 464 mg) and dimethyl acetylenedicarboxylate (1.5 mmol, 213 mg) were stirred in 50 ml of tetrahydrofuran for 24 h. When in the IR spectrum the bands of **2** were replaced by those due to **5e** the obtained purple reaction mixture was filtered over a sintered glass filter and concentrated to 40 ml. 20 ml of heptane was added and **5e** was crystallized at −80 °C. Dark purple crystals of **5e** were obtained in about 75% yield.

Reaction of 5b, c with Methyl Propynoate (MP)

A mixture of **5b** and **5c** (1 mmol, 512 mg) and MP (2 mmol, 168 mg) was stirred at 60 °C in 50 ml of toluene for 24 h. The crude reaction mixture was evaporated to dryness and separated by column chromatography. Elution with hexane/diethyl/ether (4:1) produced a small amount of an as yet unidentified yellow compound. Elution with hexane/diethyl ether (2:3) produced a minor amount of the purple complex $Fe_2[MeOC(O)C{=}CHCH{=}CC(O)OMe](CO)_4$(i-Pr-Pyca) (**6a**). A mixture of two isomeric ferracyclopentadienyl complexes $Fe_2[MeOC(O)C{=}CHC(C(O)OMe{=}CH](CO)_4$(i-Pr-Pyca) (**6b** and **6b′**) was obtained as a purple fraction by elution with diethyl ether/dichloromethane (4:1) in about 20% yield.

Thermal Reaction of 5b, c

A mixture of **5b** and **5c** (1 mmol, 512 mg) was stirred in 50 ml of toluene at 90 °C for 3 h. The solvent was evaporated and the crude reaction mixture separated by column chromatography. Elution with hexane/diethyl ether (2:3) produced a minor amount of **6a**. Elution with diethyl ether/dichloromethane (4:1) yielded a mixture of two isomeric complexes $Fe_2[MeOC(O)C{=}CHC(C(O)OMe{=}CH]$-$(CO)_4$(i-Pr-Pyca) (**6b** and **6b′**) in about 20% yield.

Reaction of $Fe_2[\mu_2\text{-}MeOC(O)C{=}C(C(O)OMe)C(O)](CO)_5$(i-Pr-Pyca) (5d) with Dimethyl Acetylenedicarboxylate (DMADC)

A solution of **5d** (1 mmol, 570 mg) and DMADC (2 mmol, 284 mg) in 50 ml of toluene was stirred at 40 °C for 24 h. The crude reaction product was purified by column chromatography. Elution with diethyl ether/dichloromethane (4:1) produced a mixture of two isomeric brown ferracyclopentadienyl complexes $Fe_2[MeOC(O)C{=}C(C(O)OMe)C(C(O)OMe){=}CC(O)OMe](CO)_4$(i-Pr-Pyca) (**7a** and **7a′**) in 60–70% yield.

Reaction of $Fe_2[\mu_2\text{-}MeOC(O)C{=}C(C(O)OMe)C(O)](CO)_5$(2,2′-bipyridine) (5e) with Dimethyl Acetylenedicarboxylate (DMADC)

A solution of **5e** (1 mmol, 578 mg) and DMADC (2 mmol, 284 mg) in 50 ml of tetrahydrofuran were refluxed for 2 h. The obtained brown solution was evaporated to dryness and separated by column chromatography. Elution with dichloromethane/tetrahydrofuran (3:1) produced the brown complex **7b** in about 40% yield.

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*These complexes have been discussed in a previous part of this series [1].

Reaction of $Fe_2[\mu_2$-MeOC(O)C=C(C(O)OMe)C(O)]-$(CO)_5$(2,2′-bipyridine) (5e) with Methyl Propynoate (MP)

A solution of **5e** (1 mmol, 578 mg) and MP (1 mmol, 84 mg) in 50 ml of tetrahydrofuran was stirred at 40 °C for 4 h. The solvent was evaporated and the crude product was purified by column chromatography. A 1:2 mixture of **7c** and **7c′** was obtained as a brown–red fraction by elution with diethyl ether/dichloromethane (3:7) in 30–40% yield.

Crystal Structure Determination of $Fe_2[\mu_2$-MeOC(O)C=CH–C(O)]$(CO)_4$(i-Pr-Pyca) (5c)

Crystals of **5c** ($Fe_2C_{19}H_{16}N_2O_8$, $Z = 2$, $M = 512.04$) are triclinic, space group $P\bar{1}$ and have cell constants $a = 10.1428(11)$, $b = 10.7084(16)$, $c = 10.0367(10)$ Å, $\alpha = 94.368(9)°$, $\beta = 100.927(13)°$, $\gamma = 93.552(13)°$, $V \doteq 1063.99$ Å^3, $D_{calc} = 1.597$ g cm^{-3}, μ(Cu Kα) = 114.18 cm^{-1}. For the measurement a dark purple crystal with dimensions 0.15 × 0.06 × 0.25 mm was chosen. 3608 intensities [θ–2θ scan, $8.3 < 2\theta < 129.6°$, $-12 < h < 12$, $-13 < k < 13$, $-11 < l < 12$] were measured at 20 °C on a Nonius CAD4 diffractometer using graphite monochromated Cu Kα radiation. 1101 intensities were below the $2.5\sigma(I)$ level and were treated as unobserved.

The structure was solved by means of the heavy atom method. The positions of the Fe atoms were derived from an E^2-patterson synthesis. The C, N and O atomic positions were derived from a ΔF-Fourier synthesis. The positions of the H atoms were derived from a ΔF-Fourier synthesis after anisotropic refinement of the non-H atoms, and were refined isotropically. The non-H atoms were further refined anisotropically, using block-diagonal least-squares calculations. The refinement converged to a final R value of 0.036 ($R_w = 0.054$), weighting scheme $w = (8.3 + F_{obs} + 0.016F_{obs}^2)^{-1}$, for the 2507 observed absorption corrected (DIFABS) [12] reflections. The anomalous dispersion of Fe was taken into account. The calculations were performed with XRAY76 [13], the atomic scattering factors were taken from Cromer and Mann [14] and the dispersion correction factors from the International Tables for X-Ray Crystallography [15].

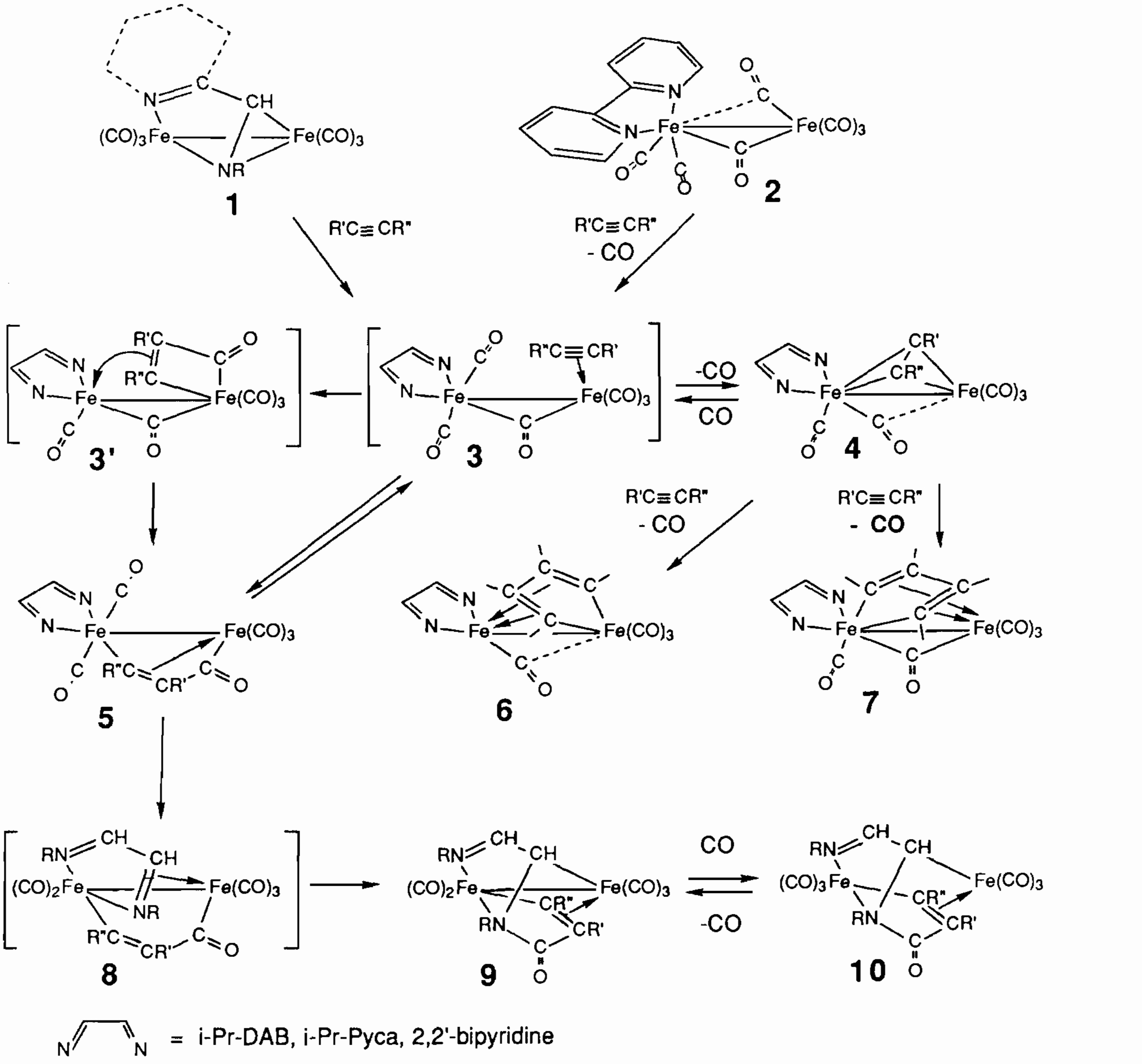
Results

In the reactions of $Fe_2(CO)_6$(i-Pr-DAB) (**1a**) with metal propynoate, $Fe_2(CO)_7$(2,2′-bipyridine) (2) with dimethyl acetylenedicarboxylate and of $Fe_2(CO)_6$(i-Pr-Pyca) (**1b**) with both alkynes the products Fe_2[Alkyne-CO]$(CO)_5$(L) (**5**) [L = R-DAB, R-Pyca, 2,2′-bipyridine; alkyne = methyl propynoate, dimethyl acetylenedicarboxylate] are formed in yields that are strongly dependent on the nature of L and the alkyne used (see Scheme 2).

Methyl propynoate reacts with **1b** to give both isomers (**5b**, **5c**) which differ with respect to the type of coupling of the alkyne to the CO. In the reaction of **1a** with MP only the isomer with the CO coupled to the substituted alkyne C atom is isolated, although in very low yield. The proposed molecular structure of the complexes **5** was derived from their NMR data. The alkyne protons in **5a** and **5b**, bonded to a C atom σ-bonded to an Fe center, resonate at low field at 9.55 and 9.48 ppm. The corresponding C atoms appear in the ^{13}C spectra in the range of 159–168 ppm, while the other π-bonded olefinic C atom is found between 44 and 51 ppm. The ketonic C atom in the complexes **5** is found at very low field between 233 and 238 ppm. The molecular structure was confirmed by the X-ray crystal structure of Fe_2[MeOC(O)C=C(H)C(O)]$(CO)_5$(i-Pr-Pyca) (**5c**). All complexes **5** are intensely blue to purple coloured, which is most likely due to strong Fe → α-diimine MLCT transitions as in many other transition metal carbonyl complexes containing a chelating α-diimine ligand [16].

Thermal reactions of the Pyca complexes **5b**, **c** did not result in the formation of the flyover complexes of type **9**, containing a ligand resulting from the coupling of the imine moiety and an alkyne to a CO ligand, as is observed in the reaction of 1a with methyl propynoate (see Scheme 1) [5]. Instead, a disproportionation reaction occurs, resulting in the formation of ferracyclopentadienyl complexes (**6**) and decomposition products. Reactions of the complexes **5** with a second equivalent of alkyne did not lead to the formation of a 'classical' flyover ligand [RC=C(R)C(O)C(R)=RC], as is observed in reactions of $Ru_2(CO)_6$(R-Pyca) [R = i-Pr, c-Hex, t-Bu] with alkynes R′C≡CH [R′ = Ph, p-Tol] to give the $Ru_2(CO)_4$(R-Pyca)[HC=C(R′)C(O)C(R′)=CH] complexes (see Scheme 1) [4]. Also in these reactions only ferracyclopentadienyl complexes $Fe_2[C_4R_2R'_2](CO)_4$(L) (**6**, **7**) were observed.

The ferracyclopentadienyl complexes (**7**) formed in the reactions of Fe_2[MeOC(O)C=C(C(O)OMe)-C(O)]$(CO)_5$(L) (**5d**, **e**) are of the type with L bonded to the Fe atom in the ferracycle and contain a bridging CO. The products (**6**) from the reactions of Fe_2[H/MeOC(O)C=C(C(O)OMe/H)C(O)]$(CO)_5$(i-Pr-Pyca) (**5b**, **c**) contain a semi-bridging CO ligand and have the Pyca ligand bonded to the Fe center which is bonded to the ferracycle (see Scheme 2). The reaction of **5e** with methyl propynoate produces an inseparable mixture of two isomers **7c** and **7c′**, Fe_2[MeOC(O)C=CHC(C(O)OMe)=CC(O)OMe]$(CO)_4$-(2,2′-bipyridine), which differ with respect to the relative positions of the bipyridine ligand and the unsubstituted C atom of the butadienyl fragment. The formation of such ferracyclopentadienyl complexes in reactions of $Fe_2(CO)_6$(L) with alkynes was the subject of a previous paper [1].



Scheme 2. Reactions of $Fe_2(CO)_6(L)$ [L = i-Pr-DAB, i-Pr-Pyca] (1a, b) and $Fe_2(CO)_7$(2,2'-bipyridine) (2) with methyl propynoate and dimethyl acetylenedicarboxylate. R' = R" = C(O)OMe; R' = H, R" = C(O)OMe. 3, 3' and 8 are proposed intermediates and have not been isolated or observed.

Crystal Structure of $Fe_2[MeOC(O)C{=}C(H)C(O)]$-$(CO)_5$(i-Pr-Pyca) (5c)

Table 4 shows the fractional coordinates and equivalent isotropic thermal parameters of the atoms of 5c. Tables 5 and 6 contain the bond lengths and angles, respectively, of the non-H atoms of 5c. Figure 1 shows a PLUTO drawing with the adopted atomic numbering. A stereoscopic ORTEP representation of 5c is given in Fig. 2.

The structure consists of an $Fe(CO)_3$ and an $Fe(CO)_2(\sigma,\sigma\text{-}N,N'$-i-Pr-Pyca) unit, which are linked by a formally single Fe–Fe bond [Fe(1)–Fe(2): 2.7191(9) Å], which is bridged by an organic ligand resulting from the coupling of a methyl propynoate molecule to a CO. The C(10) atom of the CO is σ-bonded to Fe(1) [Fe(1)–C(10): 1.936(4) Å], while the substituted alkyne C(12) atom is σ-bonded to the other Fe center [Fe(2)–C(12): 1.964(3) Å]. The former alkyne bond C(11)–C(12) is reduced to an olefinic fragment which is η^2-coordinated to Fe(1) [Fe(1)–C(11)): 2.097(3) Å; Fe(1)–C(12): 2.089(3) Å; C(11)–C(12): 1.405(5) Å]. All CO ligands are terminally bonded with normal bond lengths and angles. The Pyca ligand is chelating Fe(2) with normal Fe–N and intra-ligand bond lengths. The bridging RC=CHC(O) fragment may be compared to that of a number of complexes which have appeared in the literature in the past decade, *i.e.* Fe_2-

TABLE 4. Fractional Coordinates and Equivalent Isotropic Thermal Parameters of the Atoms of 5c

Atom	*x*	*y*	*z*	U_{eq}	Atom	*x* *x*	*y*	*z*	U_{eq}
Fe(1)	0.23721(7)	0.12168(6)	0.08266(7)	0.0370(4)	O(2)	0.3841(4)	0.3950(4)	−0.0899(4)	0.062(3)
Fe(2)	0.32887(7)	0.29756(6)	0.29556(7)	0.0323(3)	O(3)	0.2679(4)	0.4790(3)	0.0572(4)	0.055(2)
C(1)	0.5227(5)	0.1869(4)	0.4869(5)	0.040(2)	O(15)	0.0119(4)	0.2395(4)	−0.0837(4)	0.067(3)
C(2)	0.6434(5)	0.1521(5)	0.5589(6)	0.053(3)	O(16)	0.1953(5)	−0.1101(4)	−0.0998(5)	0.077(3)
C(3)	0.7597(5)	0.1804(6)	0.5106(7)	0.064(4)	O(17)	0.1092(4)	0.0190(4)	0.2916(4)	0.065(3)
C(4)	0.7528(5)	0.2432(6)	0.3958(6)	0.060(3)	O(18)	0.0595(4)	0.3827(4)	0.2281(4)	0.065(3)
C(5)	0.6291(5)	0.2729(5)	0.3272(5)	0.051(3)	O(19)	0.4309(5)	0.5589(4)	0.3573(5)	0.077(3)
C(6)	0.3990(5)	0.1805(5)	0.5381(5)	0.041(3)	H(2)	0.649(7)	0.115(7)	0.651(7)	0.10(2)
C(7)	0.1758(5)	0.2449(6)	0.5315(5)	0.051(3)	H(3)	0.849(6)	0.163(6)	0.560(6)	0.08(2)
C(8)	0.1748(7)	0.3818(7)	0.5850(6)	0.071(4)	H(4)	0.828(5)	0.266(5)	0.349(5)	0.05(1)
C(9)	0.1633(6)	0.1564(7)	0.6400(6)	0.072(4)	H(5)	0.621(5)	0.319(5)	0.243(5)	0.06(2)
C(10)	0.4213(5)	0.0800(4)	0.1392(5)	0.043(3)	H(6)	0.400(5)	0.138(5)	0.618(5)	0.06(2)
C(11)	0.4310(4)	0.1889(4)	0.0645(5)	0.039(2)	H(7)	0.102(6)	0.228(5)	0.451(6)	0.06(2)
C(12)	0.3611(4)	0.2885(4)	0.1083(4)	0.034(2)	H(11)	0.462(5)	0.185(5)	−0.020(5)	0.05(1)
C(13)	0.3412(5)	0.3904(4)	0.0127(5)	0.039(2)	H(81)	0.090(5)	0.388(5)	0.615(5)	0.06(2)
C(14)	0.2488(7)	0.5865(6)	−0.0220(7)	0.074(4)	H(82)	0.251(7)	0.407(6)	0.659(7)	0.09(2)
C(15)	0.0980(5)	0.1961(5)	−0.0162(5)	0.045(3)	H(83)	0.171(7)	0.442(7)	0.519(7)	0.10(2)
C(16)	0.2108(5)	−0.0192(5)	−0.0314(5)	0.050(3)	H(91)	0.176(6)	0.067(6)	0.612(6)	0.08(2)
C(17)	0.1619(5)	0.0652(5)	0.2132(5)	0.043(3)	H(92)	0.076(7)	0.159(6)	0.660(7)	0.10(2)
C(18)	0.1647(5)	0.3474(5)	0.2505(5)	0.045(3)	H(93)	0.219(8)	0.180(7)	0.726(8)	0.12(3)
C(19)	0.3926(5)	0.4556(5)	0.3387(5)	0.049(3)	H(141)	0.193(7)	0.631(7)	0.019(7)	0.10(2)
N(1)	0.5142(4)	0.2445(4)	0.3698(4)	0.037(2)	H(142)	0.20(1)	0.563(10)	−0.11(1)	0.17(4)
N(2)	0.2996(4)	0.2332(4)	0.4723(4)	0.036(2)	H(143)	0.352(9)	0.630(9)	−0.19(9)	0.16(4)
O(1)	0.4903(4)	−0.0001(3)	0.1861(4)	0.055(2)					

TABLE 5. Selected Bond Lengths (Å) of the Non-H Atoms of 5c[a]

Fe(1)	Fe(2)	2.7191(9)	C(1)	N(1)	1.359(4)	C(7)	N(2)	1.496(5)
Fe(1)	C(10)	1.936(4)	C(2)	C(3)	1.383(6)	C(10)	C(11)	1.442(5)
Fe(1)	C(11)	2.097(3)	C(3)	C(4)	1.370(6)	C(10)	O(1)	1.208(4)
Fe(1)	C(12)	2.089(3)	C(4)	C(5)	1.380(6)	C(11)	C(12)	1.405(5)
Fe(2)	C(12)	1.964(3)	C(5)	N(1)	1.341(5)	C(12)	C(13)	1.505(5)
C(1)	C(6)	1.443(5)	C(6)	N(2)	1.283(5)	C(13)	O(2)	1.195(4)

[a] e.s.d.s given in parentheses.

TABLE 6. Selected Bond Angles (°) of the Non-H Atoms of 5c[a]

Fe(2)	Fe(1)	C(10)	78.5(1)	Fe(1)	C(11)	C(10)	63.2(3)
Fe(2)	Fe(1)	C(11)	73.0(1)	Fe(1)	C(11)	C(12)	70.1(3)
Fe(2)	Fe(1)	C(12)	45.94(10)	C(10)	C(11)	C(12)	113.3(4)
C(10)	Fe(1)	C(11)	41.7(2)	Fe(1)	C(12)	Fe(2)	84.2(2)
C(10)	Fe(1)	C(12)	72.3(2)	Fe(1)	C(12)	C(11)	70.7(3)
C(11)	Fe(1)	C(12)	39.2(2)	Fe(1)	C(12)	C(13)	123.5(3)
Fe(1)	Fe(2)	C(12)	49.9(1)	Fe(2)	C(12)	C(11)	118.4(3)
Fe(1)	Fe(2)	N(1)	102.4(1)	Fe(2)	C(12)	C(13)	126.2(2)
Fe(1)	Fe(2)	N(2)	110.9(1)	C(11)	C(12)	C(13)	114.5(4)
C(12)	Fe(2)	N(1)	92.3(2)	Fe(2)	N(1)	C(1)	114.0(3)
C(12)	Fe(2)	N(2)	157.2(1)	Fe(2)	N(1)	C(5)	127.7(3)
N(1)	Fe(2)	N(2)	79.4(2)	C(1)	N(1)	C(5)	117.7(4)
C(1)	C(6)	N(2)	117.1(4)	Fe(2)	N(2)	C(6)	115.2(3)
Fe(1)	C(10)	C(11)	75.1(3)	Fe(2)	N(2)	C(7)	125.7(2)
Fe(1)	C(10)	O(1)	143.8(3)	C(6)	N(2)	C(7)	119.1(4)
C(11)	C(10)	O(1)	139.8(3)				

[a] e.s.d.s given in parentheses.

$(CO)_5[Ph_2PC(Ph){=}C(C(O)OEt)C{=}C(t\text{-}Bu)C(O)]$ [17], $Fe_2(CO)_6[H_2CC(Me){=}C(R)C(O)]$ (R = Et, t-Bu) [18] and $Cp_2Ru_2[PhC{=}C(Ph)C(O)]$ [19]. The bond lengths within the ligands in these complexes suggest that the actual bonding of the bridging $RC^1{=}C^2(R)\text{-}C^3(O)$ group to the dimetal core is intermediate between the case where C^1 is σ-bonded to one metal and the olefinic $C^1{=}C^2$ moiety π-bonded to the other metal, to which also the ketonic C^3 atom is σ-bonded, and the case where C^1 acts as a μ_2-methylene bridge and the ketenic C^2C^3O moiety is π-bonded via the $C^2{=}C^3$ bond. Intermediate between these extremes is a delocalized system where C^1 is σ-bonded to one metal and the $C^1{-}C^2{-}C^3$ part of the ligand bonded as an allylic system to the other metal center. The actual $C^1{=}C^2$ bond length of 1.405(5) Å in 5c, however, which in the literature complexes [17–19] is in the range of 1.38–1.42 Å, is in accordance with an η^2-coordinated olefinic bond. Also the formally

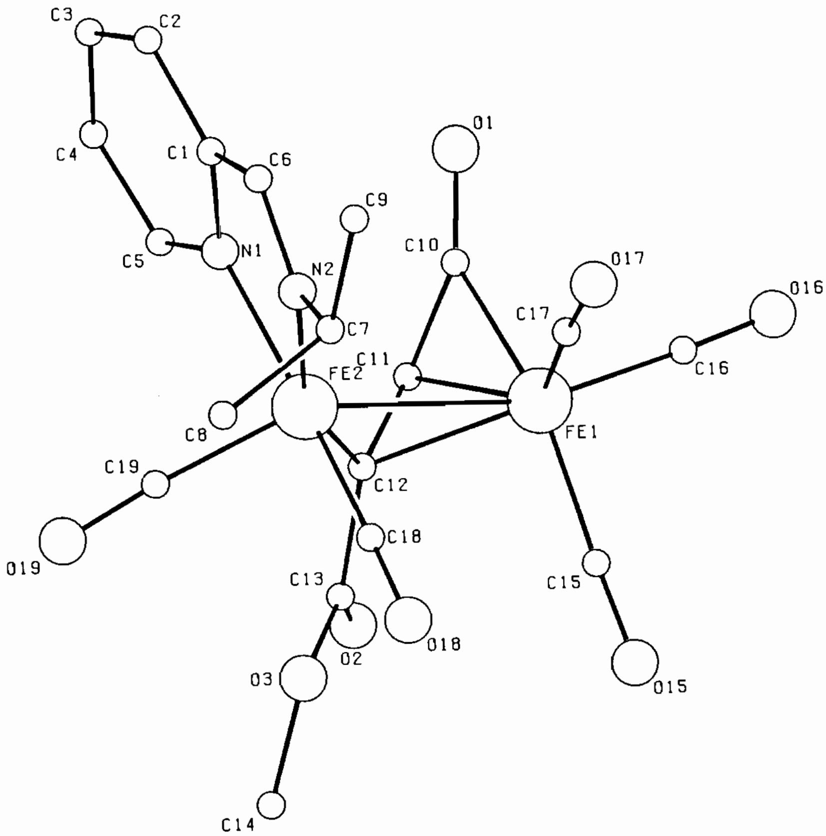


Fig. 1. PLUTO drawing of $Fe_2[\mu_2$-MeOC(O)C=CH–C(O]$(CO)_4$(i-Pr-Pyca) (5c). The H atoms are omitted for clarity.

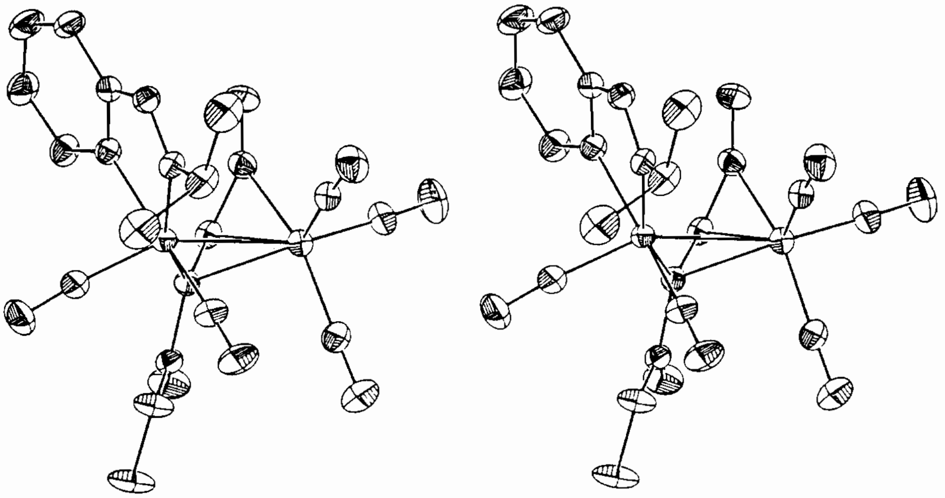


Fig. 2. Stereoscopic ORTEP representation of $Fe_2[\mu_2$-MeOC(O)C=CH–C(O)]$(CO)_4$(i-Pr-Pyca) (5c) (ellipsoid probability scale: 31%).

single C^2–C^3 bond of 1.442(5) Å in 5c, in the literature complexes [17–19] in the range of 1.45–1.50 Å, is only slightly shorter than expected for a single C–C bond. Finally the bridging C^1 atom is significantly closer to one metal than to the other, which contradicts the μ_2-methylene character. The actual bonding has consequently to be regarded as an η^2-bonded enone fragment, with some delocalization of electron density over the C^1–C^2–C^3 core, resulting in a partial allylic character.

Discussion

Formation of $Fe_2[\mu_2$-alkyne-CO$](CO)_5(L)$ (5)

We propose that the formation of the complexes $[Fe_2(\mu_2$-alkyne-CO$](CO)_5(L)$ (**5a–e**) from $Fe_2(CO)_6(L)$ [L = R-DAB, R-Pyca] (**1**) and $Fe_2(CO)_7$(2,2′-bipy) (**2**) involve the same type of intermediate $Fe_2(CO)_6(L)(\eta^2$-alkyne) (**3**) (see Scheme 2). Reaction of **1** with the alkyne results in the substitution of the η^2-bonded C=N moiety of the α-diimine by terminally η^2-C≡C bonded alkyne, resulting in **3**. The same type of intermediate results from the substitution of one of the CO ligands in **2** (most likely the semi-bridging CO) by a terminally η^2-C≡C bonded alkyne. There are two possible mechanisms via which the subsequent C–C coupling in **3** may take place. The first one involves a direct attack of the coordinated alkyne on the second Fe center and one of the CO ligands to give **5**. The second possibility is comparable to the mechanism proposed by Knox *et al.* [19] for the formation of $Cp_2Ru_2(CO)_2$[PhC=C(Ph)C(O)] and involves the initial C–C coupling of the monodentate η^2-C≡C bonded alkyne with a CO on the same metal center, producing a ferracyclobutenone fragment, π-bonded to the other Fe center (**3′**). A subsequent rearrangement involving the migration of an Fe–C σ-bond results in the formation of **5**.

Reactivity of $Fe_2[\mu_2$-alkyne-CO$](CO)_5(L)$ (5)

Heating of the enone complexes **5b–e** (with L = i-Pyca, 2,2′-bipy) or thermal reactions with alkynes did not result in the formation of flyover bridge containing complexes of the type of e.g. $Fe_2(CO)_5$[RN=C(H)C(H)N(R)C(O)C(H)=CC(O)OMe] (**9**) [5, 6] or of $Ru_2(CO)_4$(R-Pyca)[HC=C(R′)C(O)C(R′)=CH] [4]. Instead, ferracyclopentadienyl complexes of type **6** and **7** were isolated. The isolated amounts of **5a** (with L = i-Pr-DAB) were too small to study the reactivity of this complex. It is very likely that the formation of **6** and **7** is preceded by the fission of the formed C–C bond between the alkyne and the CO, to give **3** again. Such a behaviour is not unprecedented since Knox *et al.* describe the reactivity of the complexes $Cp_2M_2(CO)_2$[RC=C(R′)C(O)] (M = Fe, Ru) with a comparable bridging organic moiety, as dominated by the lability of the C–C bond between the alkyne and the CO fragment [19]. This results on the one hand in the rapid exchange of the alkyne fragment when $Cp_2Ru_2(CO)_2$[PhC=C(Ph)C(O)] is heated in the presence of another alkyne. On the other hand these complexes show a fluxional behaviour in solution which involves the rapid and reversible fission of the C–C bond between the alkyne and the ketonic CO and the concomitant formation of a C–C bond between the other alkyne C atom and one of the terminal COs. Such a dynamic behaviour is not observed for **5a–e**, but we may assume that the low stability of the C–C bond between the alkyne and the ketonic CO is in **5** comparable to that in the complexes reported by Knox *et al.* and plays an important role in the reformation of **3** from **5**.

The formation of **6** and **7** from **3** probably proceeds in the same fashion as that of the $Fe_2[C_4R_4](CO)_4(L)$ complexes which are reported in Part 4 of this series [1]. This mechanism involves the substitution of a CO on the Fe(L) center in **3** by the already terminally η^2-C≡C bound alkyne to give $Fe_2(CO)_5(L)(\mu_2,\eta^2$-alkyne) (**4**) with a μ_2,η^2-perpendicular bridging alkyne. One of such complexes, *i.e.* $Fe_2(CO)_5$(i-Pr-DAB)[μ_2,η^2-MeOC(O)C≡CC(O)OMe], of which the X-ray single crystal structure will be reported in Part 6 of this series [6], is known to react with a second equivalent of alkyne to give products of type **7**. The possibility of interconversion of **4** and **5**, via **3**, is corroborated by the observation that the isolated type **4** complex $Fe_2(CO)_5$(i-Pr-DAB)[μ_2,η^2-MeOC(O)C≡CC(O)OMe] reacts with CO with the formation of a type **9** flyover complex, most likely via intermediates of type **5** and **8** (see Scheme 2). There is no obvious explanation for the fact that the isolated complexes **5a–d** do not react further to give the flyover complexes. We can only conclude that the different pathways along which the reactions of $Fe_2(CO)_6(L)$ with alkynes may proceed have very similar activation barriers, which causes the product distribution to vary strongly with small changes in electronic and steric properties of the reactants. For **5e** the reaction path to give the flyover complex is obviously blocked, because intermediate **8** cannot be formed with 2,2′-bipy which is due to the inability of bipy to act as 6e donor. Moreover the C–C or C–N couplings which are observed for R-DAB are disfavoured in the case of 2,2′-bipy because of the loss of resonance stabilization in the pyridine ring. The observed reactivity of the 2,2′-bipy complex **5e**, however, supports our view that in the formation of ferracyclopentadienyl complexes of type **6** and **7** no intermediates are involved with 6e or 8e donating α-diimine ligands, since these coordination modes are not possible for 2,2′-bipy.

Conclusions

We have not been able to show unambiguously that the type **5** complexes are intermediates in the formation of complexes M–X=C–C(O)–C=C–M (X = C, N) with flyover ligands resulting from the coupling of an α-diimine, a CO and an alkyne, or the coupling of two alkynes and a CO. The results presented in this paper, however, strongly suggest that the type **5** complexes are involved in at least the formation of the flyover complex **9**. Furthermore, the complex $Fe_2(CO)_6(\sigma,\sigma\text{-}N,N'\text{-}L)(\eta^2\text{-alkyne})$ (3) is most likely a key intermediate in the reactions of dinuclear α-diimine carbonyl complexes with alkynes. Finally, the formation of ferracyclopentadienyl complexes from the 2,2′-bipyridine complex **5e** shows that the formation of the similar dinuclear ferracyclopentadienyl R-DAB and R-Pyca complexes in reactions of $Fe_2(CO)_6(L)$ with alkynes does not involve intermediates with a 6e or 8e bonded α-diimine ligand, as these coordination modes can be excluded for 2,2′-bipyridine.

Supplementary Material

A table of anisotropic thermal parameters of the non-H atoms, full listings of bond lengths and angles of all atoms and a listing of calculated *versus* observed structure factors (16 pages) can be ordered from the authors.

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