handling techniques. After transfer, the crystal was cooled to –159 °C for characterization and data collection. A systematic search of a limited hemisphere located a set of diffraction maxima with monoclinic symmetry and extinction corresponding to the unique space group $P2_1/a$ (alternate setting of $P2_1/c$). Subsequent solution and refinement of the structure confirmed this choice.

The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques and refined by a blocked full-matrix least squares. Hydrogen atoms were present in a difference Fourier phased on the non-hydrogen parameters and were included in the final cycles. Their positions are poorly determined as seen by the scatter in the C–H distances and angles but are qualitatively correct.

Since the crystal was nearly equidimensional, no absorption correction was performed (μ = 48.8 cm^{-1}).

Reactions of (*N*,*N'*-Diisopropyl-1,4-diaza-1,3-butadiene)ironruthenium Hexacarbonyl with Alkynes[1]

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FeRu(CO)$_6$(*i*-Pr-DAB) (1) [R-DAB = RN=CHCH=NR] reacts at 20 °C with dimethyl acetylenedicarboxylate in heptane solution to give the complexes FeRu(CO)$_5$(*i*-Pr-DAB)[μ_2,η^2-MeOC(O)C≡CC(O)OMe] (2), with DAB chelating the Ru center and the alkyne in perpendicular bridging position, and FeRu(CO)$_5$[*i*-PrN=CHCH(N-*i*-Pr)C(C(O)OMe)=CC(O)OMe] (4) in which the alkyne is C—C coupled with the η^2-C=N coordinated imine C atom of the DAB ligand (in 1). In 4 both N atoms are bonded to Fe whereas in 1 they are bonded to Ru which suggests that the formation of 4 is preceded by an isomerization of 1 involving the migration of the η^2-C=N coordinated imine fragment from Fe to Ru. The X-ray crystal structure of 4 has been determined. Dark brown crystals of 4 (FeRuC$_{19}$H$_{22}$N$_2$O$_9$, mol wt 579.31, Z = 4) are monoclinic, space group $P2_1/a$, and have cell constants a = 14.858 (1) Å, b = 17.055 (1) Å, c = 9.4289 (8) Å, and β = 94.215 (8)°. A total of 3092 reflections (Mo Kα, μ = 12.77 cm^{-1}) were used in the refinement which converged to a final R of 0.053 (R_w = 0.096). Complex 2 shows a thermally induced (70 °C) isomerization which involves the migration of one of the isopropyl methine protons to the alkyne which is transformed into an η^1-vinyl fragment in FeRu(CO)$_5$[MeOC(O)C=CHC(O)OMe][Me$_2$C=NCHCHN-*i*-Pr] (3). Reaction of 1 at 20 °C with methyl propynoate produces a mixture of two pairs of isomeric complexes, FeRu(CO)$_5$(*i*-Pr-DAB)(μ_2-HC≡CC(O)OMe) (8, 9) and FeRu(CO)$_4$(*i*-Pr-DAB)(μ_2-HC≡CC(O)OMe) (10, 11). The isomeric complexes differ with respect to the coordination of the alkyne relative to the Fe–Ru core. In all complexes 8–11 the DAB ligand is bonded as a σ,σ-N,N', η^2,η^2-C=N,C=N' bridging 8e donor with the N atoms σ-bonded to Ru and the alkyne as a μ_2-parallel bridging ligand. In 8 and 9 a fifth CO ligand is bonded to Ru and the metal centers are at a long nonbonding distance of 3.089 (2) Å. The reaction of 10 and 11 with CO at 20 °C yields 8 and 9, respectively, in quantitative yield. Both 8 and 9 again easily lose a CO ligand when a solution of these compounds is purged with N$_2$. The X-ray crystal structure of 8 has been determined. Yellow crystals of 8 (FeRuC$_{17}$H$_{20}$N$_2$O$_7$, mol wt 521.27, Z = 8) are orthorhombic, space group *Pnab*, and have cell constants a = 15.263 (2) Å, b = 18.458 (2) Å, and c = 15.130 (2) Å. A total of 4027 reflections (Mo Kα, μ = 14.57 cm^{-1}) were used in the refinement which converged to a final R of 0.050 (R_w = 0.081). In the reaction of 1 in *n*-octane at 90 °C with ethyne four products are formed, of which three are the isomeric metallacyclopentadienyl complexes FeRu[HC=CHCH=CH](CO)$_4$(*i*-Pr-DAB) (12–14). In 14 (yield 20%) the DAB ligand is chelating Fe which is bonded to the RuC$_4$ metallacycle. In 12 and 13 (both obtained in 15–20% yield) the DAB ligand is bonded to Ru and Fe, respectively, which metal atom is also part of the metallacycle. The fourth complex (15) (yield 5%) has the composition FeRu(CO)$_6$(*i*-Pr-DAB)(C$_2$H$_2$) and probably has a flyover structure in which a CO molecule is C–C coupled to the alkyne which is N–C coupled to DAB. When the reaction is performed in refluxing heptane at 98 °C, FeRu(CO)$_4$(*i*-Pr-DAB(8e))(μ_2-HC≡CH) (6) is also formed in 5–10% yield. It is shown that the product distribution of reactions of complexes M$_2$(CO)$_6$(α-diimine) with alkynes is largely determined by the nature of the η^2-C=N—M interaction.

Introduction

The formation and the chemical properties of the homodinuclear Fe and Ru carbonyl α-diimine complexes M$_2$(CO)$_6$(L) [M$_2$ = Fe$_2$, Ru$_2$; L = R-DAB (= 1,4-diaza-1,3-butadiene; RN=CHCH=NR), R-Pyca (= pyridine-2-carbaldimine; C$_5$H$_4$N-2-CH=NR)] in which the α-diimine ligand is bonded as a σ-N, μ_2-N', η^2-C=N' bridging 6e

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

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Table I. IR and FI-Mass Data and Elemental Analyses of FeRu(CO)₅(*i*-Pr-DAB)[μ₂,η²-MeOC(O)C≡CC(O)OMe] (2),
FeRu(CO)₅[MeOC(O)C=CHC(O)OMe][Me₂C=NCHCHN-*i*-Pr] (3),
FeRu(CO)₅[*i*-PrN=CHCH(N-*i*-Pr)C(C(O)OMe)=CC(O)OMe] (4), FeRu(CO)₅(*i*-Pr-DAB)(μ₂-HC≡CC(O)OMe) (8, 9),
FeRu(CO)₄(*i*-Pr-DAB)(μ₂-HC≡CC(O)OMe) (10, 11), FeRu(CO)₆(*i*-Pr-DAB)(C₂H₅) (15), and
FeRu[HC=CHCH=CH](CO)₄(*i*-Pr-DAB) (12-14), and FeRu(CO)₄(*i*-Pr-DAB)(8e))(μ₂-HC≡CH) (6)

compd	IR ν_s(C=O),^{a} cm^{-1}	FI-mass obsd (calcd)^b	elemental anal. obsd (calcd)		
			C	H	N
2	2043 (s), 2014 (vs), 1989 (m), 1970 (m), 1945 (w), 1699 (w) [hexane]	580 (579.31)	40.05 (39.39)	3.88 (3.83)	4.64 (4.84)
3	2042 (s), 2005 (s), 1982 (m), 1961 (m), 1704 (w) [hexane/CH₂Cl₂ (1:1)]	580 (579.31)	38.41 (39.39)	4.06 (3.83)	4.64 (4.84)
4	2070 (s), 2042 (vw), 2000 (vs), 1977 (s), 1932 (w), 1699 (m) [hexane/CH₂Cl₂ (1:1)]	580 (579.31)	39.69 (39.39)	4.20 (3.83)	5.1 (4.84)
6	2023 (w), 2000 (vs), 1952 (s), 1942 (s) [hexane/CH₂Cl₂]	435 (435.22)	not analyzed		
8, 9^c	2089 (m), 2028 (s), 2004 (s), 1964 (m), 1947 (s), 1683 (m) [toluene]	494 (521.27)	38.93 (39.17)	3.90 (3.87)	5.45 (5.37)
10, 11^c	2027 (w), 2004 (vs), 1963 (s), 1944 (s), 1684 (w) [toluene]	494 (493.26)	39.14 (38.96)	4.19 (4.09)	5.69 (5.68)
12	2043 (s), 1988 (vs), 1932 (vs) [hexane]	462 (461.26)	41.21 (41.66)	4.28 (4.37)	5.99 (6.07)^d
13	2019 (s), 1968 (vs), 1897 (m) [hexane]	462 (461.26)	41.21 (41.66)	4.28 (4.37)	5.99 (6.07)^d
14	2055 (s), 1993 (s), 1986 (m), 1874 (w) [hexane]	462 (461.26)	41.21 (41.66)	4.28 (4.37)	5.99 (6.07)^d
15	2092 (s), 2027 (vs), 1962 (s), 1935 (s), 1731 (m) [hexane]	492 (491.25)	not analyzed		

^{a}Solvent in square brackets. Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vs, very weak. ^{b}Based on ^{56}Fe and ^{101}Ru. ^{c}Measured as mixtures. ^{d}Elemental analysis of a mixture of 12, 13, and 14.

donor have in the recent past been studied extensively.[3] The reactivity of these complexes toward small molecules like H₂ and CO and unsaturated organic substrates such as R-DAB, R-Pyca, carbodiimides (RN=C=NR), sulfines (R₂C=S=O), ketene (H₂C=C=O), allene (H₂C=C=C-H₂), and alkynes (RC≡CR′) led to an unusually rich chemistry involving C—C, C—H, N—C, and N—H coupling reactions and metal–metal bond cleavage and formation processes.[4]

The synthesis of the heterodinuclear FeRu analogue of the above-mentioned complexes has been reported several years ago,[5] but its reactivity has as yet hardly been investigated. Recently, however, we reported the high-yield synthesis of FeRu(CO)₆(*i*-Pr-DAB),[6] which provided us with the opportunity of studying in detail the influence of the heterobimetallic nature of this complex on reactions which are known for its homodinuclear parent compounds. Because the reactions of these latter compounds with alkynes appeared to result in a wide variety of different and interesting organometallic complexes,[7] we started a study of the reactivity of FeRu(CO)₆(*i*-Pr-DAB) toward a number of different alkynes. In this paper we report the reactions of FeRu(CO)₆(*i*-Pr-DAB) with ethyne, methyl propynoate, and dimethyl acetylenedicarboxylate. We will try to relate the observed product distribution to the heterodinuclear character of the complex and compare it with that of the corresponding reactions of the diiron and diruthenium analogues.

(2) Muller, F.; van Koten, G.; Vrieze, K.; Duineveld, C. A. A.; Heijdenrijk, D.; Mak, A. N. S.; Stam, C. H. *Organometallics*, in press.

(3) (a) Staal, L. H.; Polm, L. H.; Balk, R. W.; van Koten, G.; Vrieze, K.; Brouwers, A. M. F. W. *Inorg. Chem.* 1980, *19*, 3343. (b) Frühauf, H.-W.; Landers, A.; Goddard, R.; Krüger, K. *Angew. Chem.* 1978, *90*(1), 56. (c) Polm, L. H.; van Koten, G.; Elsevier, C. J.; Vrieze, K.; van Santen, B. F. K.; Stam, C. H. *J. Organomet. Chem.* 1986, *304*, 353.

(4) (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.

(5) Keijsper, J.; Polm, L. H.; van Koten, G.; Vrieze, K.; Abbel, G.; Stam, C. H. *Inorg. Chem.* 1984, *23*, 2142.

(6) Zoet, R.; van Koten, G.; Muller, F.; Vrieze, K.; van Wijnkoop, M.; Goubitz, K.; van Halen, C. J. G.; Stam, C. H. *Inorg. Chim. Acta* 1988, *149*(2), 193.

(7) (a) Muller, F.; Vrieze, K. In *Coordination Chemistry and Catalysis*; Kiolkowski, J. J., Ed.; World Scientific Publishing Co.: Singapore, 1988. (b) Elsevier, C. J.; Muller, F.; Vrieze, K.; Zoet, R. *New J. Chem.* 1988, *12*, 571.

(8) 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=C(H)C(H)(NR)C(R′)=CR″, which is 3-amino-4-imino-1-butene.

Experimental Section

Materials and Apparatus. ¹H and ¹³C NMR spectra were recorded on Bruker AC100 and WM250 spectrometers. IR spectra were measured with a Perkin-Elmer 283 spectrometer. The Field ionization (FI) mass spectra were obtained with a Varian MAT711 double-focussing mass spectrometer with a combined EI/FI/FD source. The samples were dissolved in dichloromethane and introduced via the direct insertion probe into the ion source, of which the temperature was generally 100–150 °C. 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. FeRu(CO)₆(*i*-Pr-DAB) (1) was prepared according to known procedures.[6] CO gas, ethyne, methyl propynoate (MP), and dimethyl acetylenedicarboxylate (DMADC) were used as commercially obtained without further purification. The products were identified by IR and mass spectrometry, by elemental analyses (Table I), and by ¹H (Table II) and ¹³C NMR (Table III).

Reaction of FeRu(CO)₆(*i*-Pr-DAB) (1) with DMADC. A solution of 1 (3 mmol, 1.395 g) and DMADC (9 mmol, 1.278 g) in 100 mL of hexane was stirred during 50 h at 20 °C. The crude reaction mixture was evaporated to dryness and separated by column chromatography. Elution with hexane/diethyl ether (1:1) produced a minor amount of an as yet unidentified yellow compound. Further elution with hexane/diethyl ether (1:4) yielded the brown complex FeRu(CO)₅AIB(*i*-Pr,C(O)OMe,C(O)OMe)[8] (4) in 30% yield. Finally the purple complex FeRu(CO)₅(*i*-Pr-DAB)(μ₂,η²-DMADC) (2) was obtained in 45–50% yield by elution with diethyl ether/dichloromethane (9:1). Both complexes were further purified by recrystallization from hexane/diethyl ether (1:1) at −80 °C. When the same reaction was performed under exclusion of light, the yields of 4 and 2 are 15% and 70%, respectively. When the reaction mixture was irradiated with UV radiation (λ = 250 nm), after column chromatography 4 was obtained in 50% yield as the only product.

Thermal Conversion of FeRu(CO)₅(*i*-Pr-DAB)(μ₂,η²-DMADC) (2). A solution of 2 (1 mmol, 579 mg) in 50 mL of toluene was stirred during 5 h at 70 °C. The solvent was removed in vacuo, and the crude product was purified by column chromatography. Elution with hexane/diethyl ether (2:3) produced a small amount of an as yet unidentified brown compound. The yellow-orange complex FeRu(CO)₅[Me₂C=NCHCHN-*i*-Pr][MeOC(O)C=CHC(O)OMe] (3) was obtained by elution with hexane/diethyl ether (1:9) in about 20% yield. Orange crystals are obtained by recrystallization from hexane/diethyl ether (1:1) at −80 °C.

Reaction of FeRu(CO)₆(*i*-Pr-DAB) (1) with MP. A solution of 1 (3 mmol, 1395 mg) and methyl propynoate (3 mmol, 252 mg) in 100 mL of hexane were stirred for 60 h at 20 °C. The solvent was evaporated, and the residue was separated by column chro-

Table II. ^{1}H NMR Data of FeRu(CO)$_5$(i-Pr-DAB)[μ_2,η^2-MeOC(O)C≡CC(O)OMe] (2), FeRu(CO)$_5$[MeOC(O)C=CHC(O)OMe][Me$_2$C=NCHCHN-i-Pr] (3), FeRu(CO)$_5$[i-Pr-N=CHCH(N-i-Pr)C(C(O)OMe)=CC(O)OMe] (4), FeRu(CO)$_5$(i-Pr-DAB)(μ_2-HC≡CC(O)OMe) (8, 9), FeRu(CO)$_4$(i-Pr-DAB)(μ_2-HC≡CC(O)OMe) (10, 11), FeRu(CO)$_6$(i-Pr-DAB)(C$_2$H$_2$) (15), FeRu[HC=CHCH=CH](CO)$_4$(i-Pr-DAB) (12-14), and FeRu(CO)$_4$(i-Pr-DAB)(8e))(μ_2-HC≡CH) (6)^a

2	1.24, 1.51 (6 H, 6 H; d, d, 6 Hz; i-Pr Me); 3.91, 4.43 (1 H, 1 H; sept, sept, 6 Hz; i-Pr CH); 3.74, 3.90 (3 H, 3 H; s, s; OMe); 7.95, 8.41 (1 H, 1 H; s, s; N=CH)^a
3	1.56, 1.62 (3 H, 3 H; d, d, 6 Hz; i-Pr Me); 2.04, 2.07 (3 H, 3 H; s, s; N=CMe$_2$); 3.77 (1 H, sept, 6 Hz; i-Pr CH); 3.63, 3.86 (3 H, 3 H; s, s; OMe); 4.20, 6.77 (1 H, 1 H; d, d, 1 Hz; NCHCHN); 5.20 (1 H, s, C=CH)^a
4	0.60, 1.00 (3 H, 3 H; d, d, 6 Hz; i-Pr Me); 1.02, 1.21 (3 H, 3 H; d, d, 6 Hz; i-Pr Me); 2.22, 3.80 (1 H, 1 H; sept, sept, 6 Hz; i-Pr CH); 3.64, 3.72 (3 H, 3 H; s, s; OMe); 4.86 (1 H, s; NCH); 7.60 (1 H, s; N=CH)^a
6	0.74 (6 H, d, 6.3 Hz; i-Pr Me); 1.24 (6 H, d, 6.3 Hz; i-Pr CH); 2.16 (2 H, sept, 6.3 Hz; i-Pr CH); 6.03 (2 H, s; N=CH); 7.74 (1 H, s; HC=CH); 8.56 (1 H, s; HC=CH)^b
8	0.72, 1.02 (6 H, 6 H; d, d, 6 Hz; i-Pr Me); 1.84 (2 H, sept, 6 Hz; i-Pr CH), 3.81 (3 H, s; OMe); 5.99 (2 H, s; N=CH); 11.87 (1 H, s; C=CH)^b
9	0.72, 1.02 (6 H, 6 H; d, d, 6 Hz; i-Pr Me); 1.84 (2 H, sept, 6 Hz; i-Pr CH), 3.79 (3 H, s; OMe); 6.02 (2 H, s; N=CH); 9.95 (1 H, s; C=CH)^b
10	0.65, 1.21 (6 H, 6 H; d, d, 6 Hz; i-Pr Me); 2.15 (2 H, sept, 6 Hz; i-Pr CH); 3.83 (3 H, s; OMe); 6.10 (2 H, s; N=CH); 9.32 (1 H, s; C=CH)^b
11	0.65, 1.21 (6 H, 6 H; d, d, 6 Hz; i-Pr Me); 2.15 (2 H, sept, 6 Hz; i-Pr CH); 3.88 (3 H, s; OMe); 6.13 (2 H, s; N=CH); 10.39 (1 H, s; -C=CH-)^b
12	1.0-1.2 (6 H; i-Pr Me); 3.65 (2 H, sept, 6 Hz; i-Pr CH), 6.02, 6.60 (1 H, 1 H, d/d, d/d, 4 Hz/2 Hz; HC=CH); 7.32 (2 H, s; N=CH)^d
13	1.05, 1.14 (1 H, 1 H, 6 H, 6 H; d, d, 6 Hz; i-Pr Me); 4.09 (2 H, sept, 6 Hz; i-Pr CH); 6.02 (4 H, s(b); HC=CH); 7.75 (2 H, s; N=CH)^d
14	0.90, 1.08 (6 H, 6 H; d, d, 6 Hz; i-Pr Me); 3.62 (2 H, sept, 6 Hz; i-Pr CH); 6.06, 6.50 (d/d, d/d, 4 Hz/2 Hz; HC=CH); 7.60 (2 H, s; N=CH)^d
15	0.33, 0.76, 0.92, 0.95 (4 × 3 H, 4 × d, 6 Hz; i-Pr Me); 1.88 (1 H, d, 2 Hz; NCH); 2.60, 2.90 (1 H, 1 H; sept, sept, 6 Hz; i-Pr CH); 3.85, 4.13 (1 H, 1 H, d, d, 6 Hz; HC=CH); 6.34 (1 H, d, 2 Hz; N=CH)^e

^{a} Values in ppm relative to Me$_4$Si, spectrometer frequency: 100 MHz. ^{b} Measured in CDCl$_3$ solution, 293 K. ^{c} Measured in CDCl$_3$ solution, 273 K. ^{d} Measured in toluene-d_8 solution, 243 K. ^{e} Measured in C$_6$D$_6$ solution, 293 K.

Table III. ^{13}C NMR Data of FeRu(CO)$_5$(i-Pr-DAB)[μ_2,η^2-MeOC(O)C≡CC(O)OMe] (2), FeRu(CO)$_5$[MeOC(O)C=CHC(O)OMe][Me$_2$C=NCHCHN-i-Pr] (3), FeRu(CO)$_5$[i-PrN=CHCH(N-i-Pr)C(C(O)OMe)=CC(O)OMe] (4), FeRu(CO)$_5$(i-Pr-DAB)(μ_2-HC≡CC(O)OMe) (8), FeRu(CO)$_4$(i-Pr-DAB)(μ_2-HC≡CC(O)OMe) (10), FeRu(CO)$_6$(i-Pr-DAB)(C$_2$H$_2$) (15), and FeRu[HC=CHCH=CH](CO)$_4$(i-Pr-DAB) (12-14)^a

2	20.9, 23.91, 24.3, 26.4 (i-Pr Me); 52.2, 52.5 (OMe); 58.3, 66.0 (i-Pr CH); 75.1, 78.7 (C≡C); 155.4, 156.2 (N=CH); 167.3, 175.2 (C(O)O); 191.0 (3 × CO); 196.7 (2 × CO)^b
3	21.3, 24.8 (i-Pr Me); 27.7, 31.1 (N=CMe$_2$); 51.2, 51.3 (OMe); 64.3 (i-Pr CH); 72.3, 99.8 (NCHCHN); 121.5 (RC=CHR); 162.2 (RC=CHR); 171.0 (N=CMe$_2$); 172.0, 177.6 (C(O)O); 197.5, 199.9 (CO); 213.9 (3 × CO)^b
4	23.7, 23.8 (2×), 25.2 (i-Pr Me); 52.0, 52.5 (OMe); 62.3, 64.1 (i-Pr CH); 64.0 (CR=CRRu); 74.5 (NCH); 170, 175.9 (C(O)O); 172.0 (N=CH); 187.9, 190.0, 194.7, 199.2, 212.2 (CO); 212.4 (CR=CRRu)^c
8	25.3, 25.6 (i-Pr Me); 52.2 (OMe); 60.1 (i-Pr CH); 104.4 (N=CH); 166.0 (HC=CR); 168.8 (C(O)O); 185.3 (CO); 197.8 (CO); 200.1 (HC=CR); 211.0 (CO)^d
10	25.2, 28.8 (i-Pr Me); 52.4 (OMe); 61.8 (i-Pr CH); 99.2 (N=CH); 136.4 (HC=CR), 137.0 (HC=CR); 165.7 (C(O)O); 202.5 (CO Ru); 213.4 (CO Fe)^d
12	24.3, 25.3 (i-Pr Me); 63.9 (i-Pr C); 114.4 (C=CC=C); 151.1 (C=CC=C); 155.4 (N=CH); 215.5 (CO)^g
13	23.5, 25.3 (i-Pr Me); 58.3 (i-Pr CH); 110.9 (C=CC=C); 146.9 (C=CC=C); 152.5 (N=CH); 203.1 (CO Ru); 218.9 (μ-CO)^g
14	23.2, 26.4 (i-Pr Me); 62.8 (i-Pr CH); 115.6 (C=CC=C); 135.0 (C=CC=C); 150.6 (N=CH); 196.6, 197.5 (CO Ru); 227.9 (CO Fe)^f
15	19.2, 23.2, 24.3 (2×) (i-Pr Me); 62.2, 65.5 (i-Pr CH); 47.8, 51.4 (HC=CH); 54.5 (N-CH); 170.0 (N=CH); 178.6, 181.1, (184.4), 187.4, 192.4, 194.6 (CO), 214.6 (C=O)^e H

^{a} Values in ppm, relative to Me$_4$Si. ^{b} Measured in CDCl$_3$ solution, 273 K, spectrometer frequency (SF) = 63 MHz. ^{c} Measured in CDCl$_3$ solution, 293 K, SF = 25 MHz. ^{d} Measured in CDCl$_3$ solution, 273 K, SF = 25 MHz. ^{e} Measured in CD$_2$Cl$_2$ solution, 293 K, SF = 63 MHz. ^{f} Measured in toluene d$_8$ solution, 243 K, SF = 25 MHz. ^{g} Measured in toluene-d_8 solution, 253 K, SF = 25 MHz.

matography. A small amount of unreacted 1 was obtained by elution with hexane/diethyl ether (9:1). A yellow fraction containing a mixture of FeRu(CO)$_5$(i-Pr-DAB)(μ_2-HC≡CC(O)OMe) (8, 9) and FeRu(CO)$_4$(i-Pr-DAB)(μ_2-HC≡CC(O)OMe) (10, 11) was eluted with hexane/diethyl ether (1:1) with a total yield of 50–60%. The yield ratio 8, 9/10, 11 varied from 1:2 to 2:1 whereas the 8, 10/9, 11 ratio was generally about 3:1 but sometimes as large as 20:1. Attempts to separate these four products by further chromatography were not successful. When the reaction was performed under UV irradiation (λ = 250 nm), no changes in the relative yields were observed although some decomposition occurred and the reaction rate decreased.

Interconversion of FeRu(CO)$_5$(i-Pr-DAB)(μ_2-HC≡CC-(O)OMe) (8, 9) and FeRu(CO)$_4$(i-Pr-DAB)(μ_2-HC≡CC(O)-OMe) (10, 11). A solution of the 3:1 mixture of the two complexes FeRu(CO)$_4$(i-Pr-DAB)(μ_2-HC≡CC(O)OMe) (10, 11) was purged with CO for 1 h at 20 °C. The ν_s(C=O) region of the IR spectrum of the reaction mixture showed a virtually quantitative conversion into FeRu(CO)$_5$(i-Pr-DAB)(μ_2-HC≡CC(O)OMe) (8, 9). When a solution of 8, 9 was purged with N$_2$ for half an hour at 20 °C, the reverse reaction proceeded and a mixture of the corresponding complexes 10, 11 was formed again in quantitative yield. These

methods can also be employed to obtain, from the column chromatography fraction of the product mixture resulting from the reaction of 1 with MP, only the complexes 10, 11 or the complexes 8, 9. The mixtures 8, 9 and 10, 11 were recrystallized from hexane at −30 °C, which produced yellow crystals. From a mixture of crystals of 8 and 9 one was chosen for an X-ray crystal structure determination which showed it to contain complex 8.

Reaction of FeRu(CO)$_6$(i-Pr-DAB) (1) with Ethyne. A solution of 1 (3 mmol, 1395 mg) in 100 mL of *n*-octane was purged with ethyne at 90 °C for 2 hours during which the brown-red color of the solution changed to purple. The crude reaction mixture was evaporated to dryness and separated by column chromatography. An intensely colored purple fraction was obtained by elution with hexane/diethyl ether (9:1). This solution was concentrated to 60 mL, and at −30 °C a mixture of orange crystals of FeRu(CO)$_6$(i-Pr-DAB)(C$_2$H$_2$) (15) (yield 5%) and purple crystals of FeRu[HC=CHCH=CH](CO)$_4$(i-Pr-DAB) (14) (yield 20%) precipitated. The mother liquor was concentrated to 40 mL from which at −30 °C a mixture of crystals of 12 and 13 (both FeRu[HC=CHCH=CH](CO)$_4$(i-Pr-DAB)) was obtained, both in 15–20% yield. When the reaction of 1 with ethyne was performed in refluxing heptane at 98 °C, concentrating the chro-

Table IV. Crystallographic Data of FeRu(CO)$_5$[i-PrN=CHCH(N-i-Pr)C(C(O)OMe)=CC(O)OMe] (4) and FeRu(CO)$_5$(i-Pr-DAB)(μ_2-HC=CC(O)OMe) (8)

	4	8
formula, mol wt	FeRuC$_{19}$H$_{22}$N$_2$O$_9$, 579.31	FeRuC$_{17}$H$_{20}$N$_2$O$_7$, 521.27
cryst system	monoclinic	orthorhombic
space group	$P2_1/a$	$Pnab$
a, Å	14.858 (1)	15.263 (2)
b, Å	17.055 (1)	18.458 (2)
c, Å	9.4289 (8)	15.130 (2)
α, deg	90	90
β, deg	94.215 (9)	90
γ, deg	90	90
V, Å^3	2383	4262
d_{calcd}, g·cm^{-1}, Z	1.62, 4	1.62, 8
μ, cm^{-1}	12.77	14.57
cryst color, size, mm^3	brown, 0.15 × 0.8 × 0.25	yellow, 0.3 × 0.3 × 0.3
radiatn	Mo Kα, λ = 0.71069 Å	Mo Kα, λ = 0.71069 Å
2θ range, deg	1.1–30	3.48–69.8
no. of reflctns	7154	10141
no. of $I < 2.5\sigma(I)$	4062	6067
no. of reflctns in refinement	3092	4027
h min, max	−20, 20	0, 23
k min, max	0, 23	0, 29
l min, max	0, 13	0, 24
absorptn corr	DIFABS[10]	DIFABS[10]
extinctn corr	isotropic	no
weighting scheme	$w = 1/(5.12 + F_o + 0.0145F_o{}^2)$	$w = 1/(5.76 + F_o + 0.0135F_o{}^2)$
anomalous scattering	Fe, Ru	Fe, Ru
final R, R_w	0.053, 0.096	0.050, 0.081

matography fraction produced in 5–10% yield the complex FeRu(CO)$_4$(i-Pr-DAB(8e))(μ_2-HC=CH) (6). After 6 was collected by filtration, cooling the purple solution as described above also yielded complexes 12–15.

Crystal Structure Determinations of FeRu(CO)$_5$[i-PrN=CHCH(N-i-Pr)C(C(O)OMe)=CC(O)OMe] (4) and FeRu(CO)$_5$(i-Pr-DAB)(μ_2-HC=CC(O)OMe) (8). The details of the crystal structure determination of compounds 4 and 8 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 8 were located by using an E^2 Patterson synthesis and those of 4 by using the symbolic addition program set SIMPEL.[9] The C, N, and O atomic positions were derived from ΔF Fourier syntheses. The positions of the H atoms of 4 were calculated and not refined and those of 8 were calculated and refined isotropically. The refinement of the non-H atoms proceeded by using anisotropic block-diagonal least-squares calculations. An empirical absorption correction (DIFABS)[10] was applied. The calculations were performed with XRAY76,[11] the atomic scattering factors were taken from Cromer and Mann (1968),[12] and the dispersion correction factors were taken from ref 13.
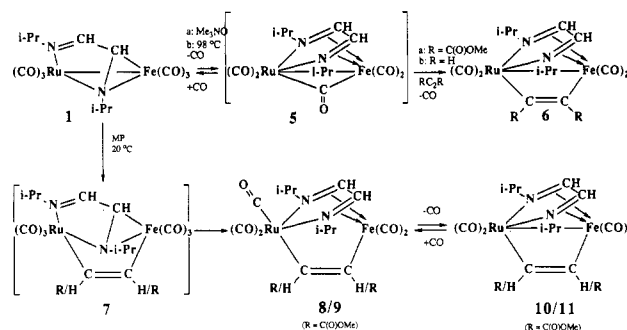
Results and Discussion

FeRu(CO)$_6$(i-Pr-DAB) (1) reacts at 20 °C with dimethyl acetylenedicarboxylate in hexane solution to give two products: FeRu(CO)$_5$(i-Pr-DAB)[μ_2,η^2-MeOC(O)C=CC(O)OMe] (2) and FeRu(CO)$_5$[i-Pr-N=CHCH(N-i-Pr)C-(C(O)OMe)=CC(O)OMe] (4) (see Scheme I). The yields

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

(10) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(11) Stewart, J. M. The XRAY76 system, Tech. Rep. TR446; Computer Science Center, University of Maryland, College Park, MD, 1976.

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

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

Scheme I. Reactions of FeRu(CO)$_6$(i-Pr-DAB) with DMADC
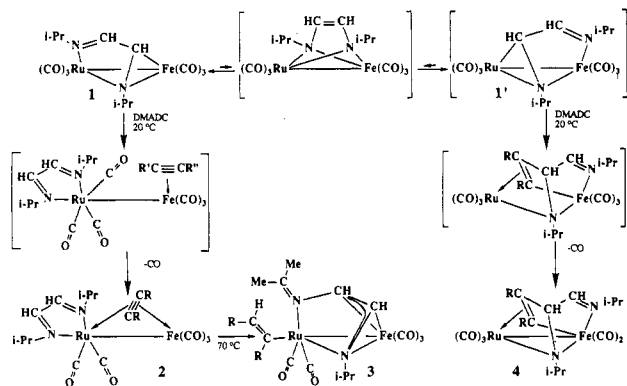
Scheme II. Formation of 6 and 8–11

depend particularly on whether or not the reaction was performed under the exclusion of light, see Experimental Section. Complex 2 is isostructural with the diiron complex Fe$_2$(CO)$_5$(i-Pr-DAB)[μ_2,η^2-MeOC(O)C=CC(O)OMe], of which the synthesis and structure were reported recently.[2] Complex 2 consists of an Ru(CO)$_2$(σ,σ-N,N'-i-Pr-DAB) unit and an Fe(CO)$_3$ unit which are bridged by a μ_2,η^2-perpendicular bridging DMADC molecule. In Fe$_2$(CO)$_5$(i-Pr-DAB)[μ_2,η^2-MeOC(O)C=CC(O)OMe] one of the CO ligands on the Fe center to which the DAB is bonded is semi-bridging, which is reflected in the ν_s(C=O) frequency of 1896 cm^{-1}. The lowest CO frequency in 2 is 1945 cm^{-1} which indicates that no semibridging CO ligand is present.

Upon heating to 70 °C in toluene solution, 2 is converted in low yield into FeRu(CO)$_5$[Me$_2$C=NCHCHN-i-Pr]-[MeOC(O)C=CHC(O)OMe] (3). In this complex the methine proton of one of the DAB i-Pr groups has migrated to one of the alkyne C atoms which is converted into an η^1-vinyl fragment bonded to Ru, to which also both N atoms are coordinated. A similar thermally induced isomerization of the diiron analogue Fe$_2$(CO)$_5$(i-Pr-DAB)[μ_2,η^2-MeOC(O)C=CC(O)OMe] was reported recently, along with the crystal structure of diiron analogue of 3, Fe$_2$(CO)$_5$[Me$_2$C=N-CHCHN-i-Pr][η^1-MeOC(O)C=CHC(O)OMe].[2] The assumption that in 3 the Ru center is bonded to both N atoms is based on the observation that also in 2 the i-Pr-DAB ligand is bonded to Ru and that during the isomerization no migration of the ligand from Ru to Fe is expected.

The molecular structure of FeRu(CO)$_5$AIB(i-Pr,C(O)-OMe,C(O)OMe) (4) consists of a Ru(CO)$_3$ and an Fe(CO)$_2$ center which are bridged by an AIB ligand[8] resulting from the C–C coupling of the alkyne to one of the imine C atoms of the DAB ligand. Both N atoms of the AIB ligand are bonded to the Fe center. This molecular structure was confirmed by an X-ray crystal structure determination, which will be discussed below.

The reaction of 1 at 20 °C with MP in hexane solution produces a mixture of two complexes FeRu(CO)$_5$(i-Pr-DAB)(μ_2-HC≡CC(O)OMe) (8, 9) and two complexes FeRu(CO)$_4$(i-Pr-DAB)(μ_2-HC≡CC(O)OMe) (10, 11) (see Scheme II). The isomeric complexes differ with respect to the coordination of the μ_2-bridging alkyne relative to the FeRu(CO)$_4$(i-Pr-DAB) fragment. The formation of such type of isomers was also observed in the reaction of Ru$_2$(CO)$_6$(i-Pr-DAB) with phenylacetylene in which two isomers of Ru$_2$(CO)$_4$(i-Pr-DAB)(μ_2-phenylacetylene) were found.[14] The relative yield of the complexes with the CC(O)OMe moiety of the alkyne bonded to Ru (8, 10) and those with the CH moiety bonded to Ru (9, 11) varies strongly from about 3:1 to about 20:1. We have not been able to determine what is the cause of this varying product distribution. Irradiation of the reaction mixture with UV light (λ = 250 nm) has no influence on the product distribution.

In all four complexes 8–11 the DAB ligand in bonded as a σ,σ-N,N', η^2,η^2-C=N,C=N' bridging 8e donor, with both N atoms σ-bonded to Ru. In complexes 8 and 9 the Ru center has three terminal CO ligands, whereas in 10 and 11 there are two terminal CO ligands on Ru. The second major difference between the two sets of isomers concerns the absence of an Fe–Ru bond in 8 and 9, which became clear from the X-ray crystal structure determination of 8, which will also be discussed below. Complexes 8 and 9 easily lose one of the CO groups on Ru when a solution is purged with N$_2$ to give quantitatively complexes 10 and 11. Also the reverse reaction of 10, 11 with CO to give 8, 9 proceeds readily at room temperature in quantitative yield.

The thermal reaction of 1 with ethyne at 90 °C produces a number of products. The structure of the orange complex with the composition FeRu(CO)$_6$(i-Pr-DAB)(C$_2$H$_2$) (15) is possibly comparable to that of the previously reported flyover complexes Fe$_2$(CO)$_5$[RN=CHCHN(R)C-(O)CR'=CC(O)OMe] (R = i-Pr, c-Hex; R' = H, C(O)-OMe)[2,15] resulting from the reactions of Fe$_2$(CO)$_6$(R-DAB) with MP or DMADC. The flyover ligands in these complexes originate from the coupling of one of the DAB N atoms and one of the alkyne C atoms to a CO molecule. In the proposed structure of 15, however, the coupled CO ligand is σ-bonded to Ru and is C–C coupled to the ethyne fragment, which has formed a C–N bond with one of the DAB N atoms (see Scheme III). We have not been able to derive from the IR and ^{1}H and ^{13}C NMR data with certainty the relative positions of the Fe and Ru centers in the molecule.

The three other products of the reaction of 1 with ethyne all have the general formula FeRu[HC=CHCH=CH]-(CO)$_4$(i-Pr-DAB) and contain a σ,σ-N,N'-chelating DAB ligand and a metallacyclopentadienyl system resulting from the coupling of two ethyne molecules and one of the metal centers. The proposed structure of 14, based on the ^{13}C NMR data of the CO and ethyne C atoms (see NMR spectroscopy section), consists of an Fe(CO)(i-Pr-DAB) unit bonded to a (CO)$_3$Ru[HC=CHCH=CH] metallacycle. In 12 and 13 the DAB is bonded to the M(CO)-[HC=CHCH=CH] metallacycle, which is bonded to the M'(CO)$_3$ unit. In 12 M = Ru and M' = Fe; in 13 M = Fe and M' = Ru (see Scheme III).

Molecular Structure of FeRu(CO)$_5$AIB(i-Pr,C-(O)OMe,C(O)OMe) (4). The molecular structure of 4

Table V. Fractional Coordinates and Equivalent Isotropic Thermal Parameters of the Non-H Atoms of 4 (Esd's in Parentheses)

atom	x	y	z	U_{eq}, Å^2
Ru(1)	0.51160 (4)	0.28435 (4)	0.36102 (7)	0.0312 (3)
Fe(1)	0.44084 (7)	0.28840 (7)	0.09656 (11)	0.0315 (5)
N(1)	0.4050 (4)	0.3483 (4)	0.2651 (6)	0.030 (3)
N(2)	0.3068 (4)	0.2831 (4)	0.0552 (7)	0.040 (4)
C(1)	0.5148 (6)	0.3184 (6)	0.5551 (10)	0.052 (6)
C(2)	0.5949 (6)	0.2023 (5)	0.4257 (9)	0.043 (5)
C(3)	0.6038 (5)	0.3515 (5)	0.2953 (9)	0.043 (5)
C(4)	0.4805 (7)	0.3718 (5)	0.0037 (9)	0.045 (5)
C(5)	0.4854 (6)	0.2275 (5)	−0.0331 (9)	0.039 (5)
C(6)	0.3281 (5)	0.2996 (4)	0.3031 (8)	0.033 (4)
C(7)	0.2665 (5)	0.2896 (5)	0.1688 (9)	0.039 (4)
C(8)	0.3924 (6)	0.4348 (5)	0.2705 (10)	0.042 (5)
C(9)	0.3811 (7)	0.4641 (6)	0.4222 (11)	0.060 (6)
C(10)	0.3153 (8)	0.4644 (6)	0.1714 (13)	0.067 (7)
C(11)	0.2525 (6)	0.2693 (6)	−0.0793 (10)	0.057 (6)
C(12)	0.2496 (9)	0.1837 (8)	−0.1134 (13)	0.088 (9)
C(13)	0.2872 (9)	0.3178 (8)	−0.2005 (12)	0.081 (8)
C(14)	0.3786 (5)	0.2228 (5)	0.3396 (8)	0.032 (4)
C(15)	0.4317 (5)	0.2010 (4)	0.2288 (8)	0.031 (4)
C(16)	0.4568 (6)	0.1188 (5)	0.2007 (9)	0.041 (5)
C(17)	0.3948 (10)	−0.0038 (6)	0.1299 (17)	0.096 (10)
C(18)	0.3453 (5)	0.1713 (5)	0.4507 (9)	0.038 (4)
C(19)	0.3761 (9)	0.0547 (7)	0.5844 (13)	0.078 (8)
O(1)	0.5191 (7)	0.3378 (6)	0.6719 (8)	0.100 (7)
O(2)	0.6393 (4)	0.1533 (4)	0.4666 (8)	0.063 (4)
O(3)	0.6549 (5)	0.3945 (5)	0.2569 (9)	0.075 (5)
O(4)	0.5101 (7)	0.4224 (4)	−0.0588 (8)	0.085 (6)
O(5)	0.5130 (5)	0.1876 (4)	−0.1171 (7)	0.064 (4)
O(6)	0.5312 (4)	0.0923 (4)	0.1951 (8)	0.057 (4)
O(7)	0.3816 (4)	0.0768 (3)	0.1691 (8)	0.059 (4)
O(8)	0.2758 (4)	0.1804 (4)	0.5052 (7)	0.057 (4)
O(9)	0.4025 (4)	0.1126 (4)	0.4825 (7)	0.054 (4)

Table VI. Selected Bond Lengths (Å) of the Non-H Atoms of 4 (Esd's in Parentheses)

Ru(1)–Fe(1)	2.6350 (9)	Fe(1)–C-(15)	1.955 (5)	C(6)–C(14)	1.535 (8)
Ru(1)–N-(1)	2.075 (4)	N(1)–C(6)	1.478 (7)	C(14)–C(15)	1.405 (7)
Ru(1)–C-(14)	2.234 (5)	N(1)–C(8)	1.490 (7)	C(14)–C(18)	1.480 (8)
Ru(1)–C-(15)	2.183 (5)	N(2)–C(7)	1.270 (7)	C(15)–C(16)	1.479 (8)
Fe(1)–N(1)	1.994 (4)	N(2)–C-(11)	1.471 (8)	C(16)–O(6)	1.199 (8)
Fe(1)–N(2)	2.002 (4)	C(6)–C(7)	1.517 (8)	C(18)–O(8)	1.196 (7)

consists of a Ru(CO)$_3$ fragment and an Fe(CO)$_2$ fragment (all CO ligands terminally bonded with normal bond lengths and angles) which are linked by a formally single Fe–Ru bond of 2.6350 (9) Å. This bond length may well be compared to that in other dinuclear FeRu carbonyl complexes with a formally single Fe–Ru bond, e.g. FeRu-(CO)$_6$(i-Pr-DAB) (1) with Fe–Ru = 2.6602 (9) Å.[6] The metal carbonyl core is bridged by a formally eight-electron donating organic ligand resulting from the C–C coupling of one of the imine C atoms and one of the alkyne C atoms. The formation of such AIB ligands was already known from the reactions of Ru$_2$(CO)$_6$(R-DAB), which is isostructural to 1, with alkynes.[16] In 4 this ligand is bonded to Fe via two σ-N donor bonds [Fe–N(1) = 1.994 (4) Å; Fe–N(2) = 2.002 (4) Å] and via an Fe–C bond with the alkyne C(15) atom [Fe–C(15) = 1.955 (5) Å]. The alkyne C(14)–C(15) bond is reduced to an olefinic fragment [C-(14)–C(15) = 1.405 (7) Å] which is π-bonded to Ru [Ru-C(14) = 2.234 (5) Å; Ru–C(15) = 2.183 (5) Å]. Finally N(1) is σ-bonded to Ru [Ru–N(1) = 2.075 (4) Å]. The most striking structural difference with the Ru$_2$(CO)$_5$AIB(R,-

(14) Part 1 of this series: Muller, F.; van Koten, G.; Vrieze, K.; Heijdenrijk, D. *Inorg. Chim. Acta* 1989, *158*, 69.

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

(16) Staal, L. H.; van Koten, G.; Vrieze, K.; van Santen, B.; Stam, C. H. *Inorg. Chem.* 1981, *20*, 3598.
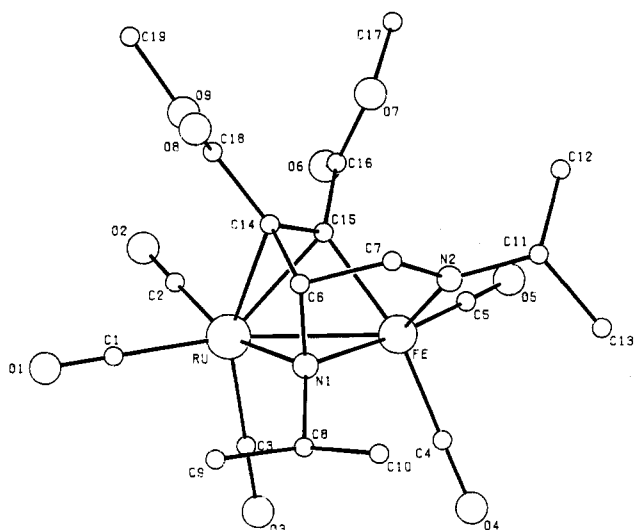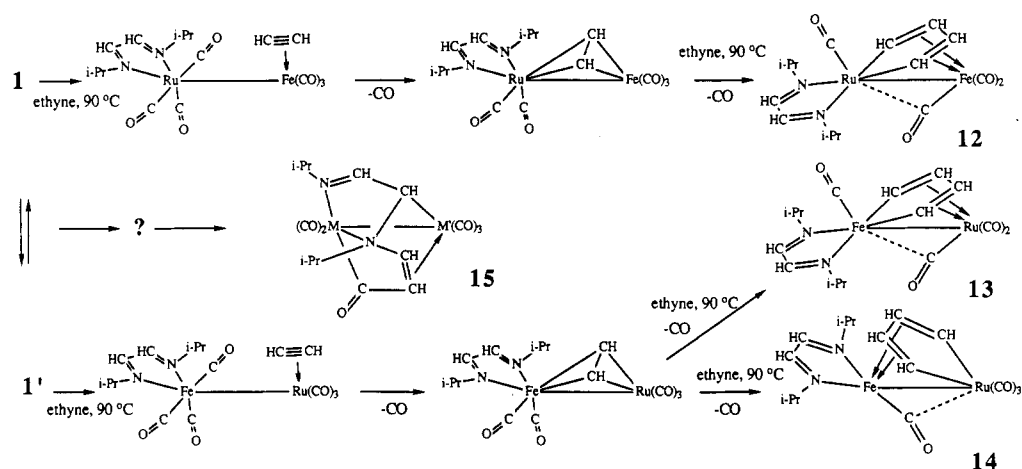
Scheme III. Reaction of FeRu(CO)₆(i-Pr-DAB) with Ethyne

Figure 1. PLUTO drawing of FeRu(CO)₅[i-PrN=CHCH(N-i-Pr)C(C(O)OMe)=CC(O)OMe] (4). The H atoms are omitted for clarity.

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

Fe(1)–Ru(1)–N(1)	48.3 (1)	Fe(1)–N(2)–C(11)	130.5 (4)
Fe(1)–Ru(1)–C(14)	68.8 (2)	C(7)–N(2)–C(11)	118.5 (7)
Fe(1)–Ru(1)–C(15)	46.7 (2)	N(1)–C(6)–C(7)	106.9 (6)
N(1)–Ru(1)–C(14)	64.2 (3)	N(1)–C(6)–C(14)	99.2 (6)
N(1)–Ru(1)–C(15)	74.2 (3)	C(7)–C(6)–C(14)	110.3 (6)
C(14)–Ru(1)–C(15)	37.1 (2)	N(2)–C(7)–C(6)	114.9 (6)
Ru(1)–Fe(1)–N(1)	51.0 (1)	Ru(1)–C(14)–C(6)	92.0 (4)
Ru(1)–Fe(1)–N(2)	120.3 (2)	Ru(1)–C(14)–C(15)	69.5 (4)
Ru(1)–Fe(1)–C(15)	54.4 (2)	Ru(1)–C(14)–C(18)	123.7 (4)
N(1)–Fe(1)–N(2)	81.8 (3)	C(6)–C(14)–C(15)	110.6 (6)
N(1)–Fe(1)–C(15)	81.2 (3)	C(6)–C(14)–C(18)	118.8 (6)
N(2)–Fe(1)–C(15)	88.6 (3)	C(15)–C(14)–C(18)	127.2 (5)
Ru(1)–N(1)–Fe(1)	80.7 (3)	Ru(1)–C(15)–Fe(1)	78.9 (3)
Ru(1)–N(1)–C(6)	100.3 (4)	Ru(1)–C(15)–C(14)	73.4 (5)
Ru(1)–N(1)–C(8)	126.9 (4)	Ru(1)–C(15)–C(16)	125.9 (4)
Fe(1)–N(1)–C(6)	99.3 (4)	Fe(1)–C(15)–C(14)	110.0 (5)
Fe(1)–N(1)–C(8)	125.2 (4)	Fe(1)–C(15)–C(16)	125.3 (4)
C(6)–N(1)–C(8)	116.6 (5)	C(14)–C(15)–C(16)	123.2 (5)
Fe(1)–N(2)–C(7)	110.9 (4)		

R′,R″) complexes is the absence of a bridging CO ligand in **4**. This is most likely caused by the different electronegativities of Fe and Ru which leads to a different bonding of the AIB ligand as a result of a different electron distribution relative to the diruthenium complexes. It is worthy to note that in **4** both N atoms are bonded to Fe whereas in the starting complex **1** both N atoms were bonded to Ru. The formation of **4** can therefore not be regarded as a simple insertion of the alkyne into the imine C–M bond of **1** but obviously involves a more complicated

rearrangement, which will be discussed in the Complex Formation section.

Molecular Structure of FeRu(CO)₅(i-Pr-DAB)(μ₂-HC≡CC(O)OMe) (8). In **8** a Ru(CO)₃ unit and an Fe(CO)₂ unit are bridged by a σ,σ-N,N′, η²,η²-C=N,-C=N′ 8e bonded DAB ligand and a μ₂-parallel bonded methyl propynoate. The DAB ligand is bonded in such a fashion that both N atoms are σ-bonded to Ru [Ru–N(1) = 2.139 (4) Å; Ru–N(2) = 2.156 (4) Å], and both C=N fragments are π-bonded to Fe [Fe–N(1) = 2.055 (4) Å; Fe–C(10) = 2.032 (5) Å; Fe–C(11) = 2.030 (6) Å; Fe–N(2) = 2.060 (4) Å]. The alkyne is bonded with the C–C(O)OMe moiety to Ru [Ru–C(6) = 2.097 (5) Å] and via the CH moiety to Fe [Fe–C(7) = 1.954 (5) Å]. The long Fe···Ru
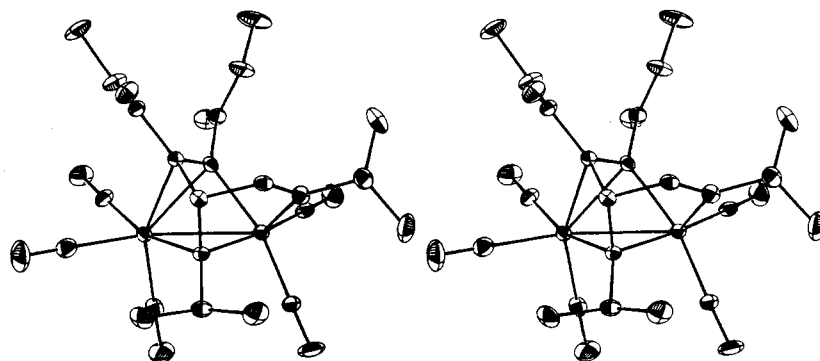
Figure 2. Stereoscopic ORTEP representation of FeRu(CO)₅[i-PrN=CHCH(N-i-Pr)C(C(O)OMe)=CC(O)OMe] (4). Ellipsoid probability scale: 30%.

Table VIII. Fractional Coordinates and Equivalent Isotropic Thermal Parameters of the Non-H Atoms of 8 (Esd's in Parentheses)

atom	x	y	z	U_{eq}, Å^2
Ru	0.43804 (4)	0.10327 (3)	0.29767 (4)	0.0350 (2)
Fe	0.41651 (8)	0.26709 (6)	0.33362 (7)	0.0422 (5)
C(1)	0.5357 (6)	0.0405 (4)	0.3166 (5)	0.049 (4)
C(2)	0.4154 (6)	0.0494 (4)	0.1935 (5)	0.049 (4)
C(3)	0.3546 (6)	0.0439 (4)	0.3736 (6)	0.052 (4)
C(4)	0.4786 (7)	0.3306 (5)	0.3923 (7)	0.062 (5)
C(5)	0.3678 (7)	0.3384 (5)	0.2759 (7)	0.062 (5)
C(6)	0.5173 (4)	0.1750 (4)	0.2258 (4)	0.033 (3)
C(7)	0.5051 (5)	0.2456 (4)	0.2441 (5)	0.042 (3)
C(8)	0.5842 (5)	0.1559 (4)	0.1578 (4)	0.039 (3)
C(9)	0.6572 (9)	0.0616 (7)	0.0799 (7)	0.084 (8)
C(10)	0.3093 (5)	0.2096 (4)	0.3712 (5)	0.044 (4)
C(11)	0.3720 (6)	0.2054 (4)	0.4352 (5)	0.048 (4)
C(12)	0.5238 (6)	0.1789 (5)	0.4757 (5)	0.053 (5)
C(13)	0.5117 (9)	0.1145 (6)	0.5363 (7)	0.076 (7)
C(14)	0.6120 (6)	0.1822 (6)	0.4349 (7)	0.071 (6)
C(15)	0.2709 (6)	0.1924 (5)	0.2172 (6)	0.058 (5)
C(16)	0.2072 (7)	0.1308 (7)	0.2220 (9)	0.076 (7)
C(17)	0.3127 (7)	0.2023 (6)	0.1274 (6)	0.070 (6)
N(1)	0.3384 (4)	0.1844 (3)	0.2882 (4)	0.040 (3)
N(2)	0.4526 (4)	0.1777 (3)	0.4065 (4)	0.038 (3)
O(1)	0.5938 (5)	0.0037 (4)	0.3276 (6)	0.080 (5)
O(2)	0.4017 (6)	0.0156 (4)	0.1328 (5)	0.085 (5)
O(3)	0.3097 (6)	0.0101 (4)	0.4138 (6)	0.092 (6)
O(4)	0.5186 (6)	0.3741 (4)	0.4307 (7)	0.089 (6)
O(5)	0.3337 (7)	0.3860 (4)	0.2391 (7)	0.101 (7)
O(6)	0.6291 (4)	0.1985 (3)	0.1168 (4)	0.057 (3)
O(7)	0.5921 (5)	0.0840 (3)	0.1449 (4)	0.060 (4)

Table IX. Selected Bond Lengths (Å) of the Non-H Atoms of 8 (Esd's in Parentheses)

Ru-C(1)	1.910 (6)	Fe-C(7)	1.954 (5)	C(4)-O(4)	1.16 (1)
Ru-C(2)	1.895 (6)	Fe-C(10)	2.032 (5)	C(5)-O(5)	1.16 (1)
Ru-C(3)	2.035 (6)	Fe-C(11)	2.030 (6)	C(6)-C(7)	1.345 (7)
Ru-C(6)	2.097 (5)	Fe-N(1)	2.055 (4)	C(6)-C(8)	1.491 (7)
Ru-N(1)	2.139 (4)	Fe-N(2)	2.060 (4)	C(10)-C(11)	1.363 (8)
Ru-N(2)	2.156 (4)	C(1)-O(1)	1.128 (8)	C(10)-N(1)	1.411 (7)
Fe-C(4)	1.750 (7)	C(2)-O(2)	1.129 (8)	C(11)-N(2)	1.402 (7)
Fe-C(5)	1.746 (7)	C(3)-O(3)	1.109 (9)		

distance of 3.089 (2) Å indicates the absence of a bonding metal–metal interaction. The structure of 8 is reminiscent of that of the earlier reported complexes Ru$_2$(CO)$_4$(i-Pr-DAB)(μ_2-HC≡CH)[17] and Fe$_2$(CO)$_4$(i-Pr-DAB)(μ_2-HC≡CC(O)OMe),[14] in which also the metal carbonyl cores are bridged by an 8e donating i-Pr-DAB ligand and a μ_2-bridging alkyne. There are, however, three important structural differences to be noticed. First, there is the third CO ligand on the metal atom (Ru) to which both N atoms are σ-bonded. Second, there is the long nonbonding metal–metal internuclear distance, and finally there is the strong deviation of the Ru atom from the plane defined by the DAB N–C–C–N skeleton, in contrast to the almost coplanar configuration of the metallacycle in the above-mentioned homodinuclear Fe$_2$ and Ru$_2$ complexes.

When one performs an electron count on 8 and considers the DAB ligand as donating four electrons to Ru and four electrons to Fe, then Ru appears to be a 19e center, while Fe has 17 valence electrons. To obey the 18e rule one has to regard the DAB ligand to be bonded to the metal carbonyl core via μ_2-N amido bridges, donating three electrons to either metal center and an olefinic central C–C bond η^2-C=C coordinated to Fe. This would also explain the deviation of the metallacycle from planarity.

In a theoretical study, however, on the electronic structure of Ru$_2$(CO)$_4$(i-Pr-DAB)(μ_2-HC≡CH) and Ru$_2$-

(17) Staal, L. H.; van Koten, G.; Vrieze, K.; Ploeger, F.; Stam, C. H. *Inorg. Chem.* **1981**, 20, 1830.
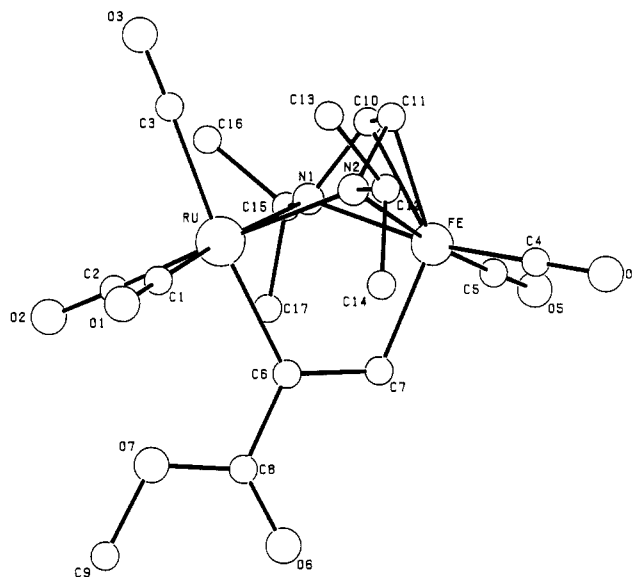
Figure 3. PLUTO drawing of FeRu(CO)$_5$(i-Pr-DAB)(μ_2-HC≡CC(O)OMe) (8). The H atoms are omitted for clarity.

Table X. Selected Bond Angles (deg) for the Non-H Atoms of 8 (Esd's in Parentheses)

C(1)-Ru-C(2)	87.1 (4)	N(1)-Fe-N(2)	74.9 (3)
C(1)-Ru-C(3)	94.4 (4)	Ru-C(6)-C(7)	115.1 (4)
C(1)-Ru-C(6)	90.6 (4)	Ru-C(6)-C(8)	127.1 (4)
C(1)-Ru-N(1)	171.8 (3)	C(7)-C(6)-C(8)	117.7 (5)
C(1)-Ru-N(2)	101.1 (3)	Fe-C(7)-C(6)	115.8 (4)
C(2)-Ru-C(3)	94.2 (4)	Fe-C(10)-C(11)	70.3 (5)
C(2)-Ru-C(6)	90.3 (3)	Fe-C(10)-N(1)	70.7 (4)
C(2)-Ru-N(1)	100.5 (3)	C(11)-C(10)-N(1)	113.1 (6)
C(2)-Ru-N(2)	171.2 (2)	Fe-C(11)-C(10)	70.5 (5)
C(3)-Ru-C(6)	173.4 (2)	Fe-C(11)-N(2)	71.1 (5)
C(3)-Ru-N(1)	88.2 (3)	C(10)-C(11)-N(2)	114.6 (7)
C(3)-Ru-N(2)	88.7 (3)	Ru-N(1)-Fe	94.9 (3)
C(6)-Ru-N(1)	86.2 (3)	Ru-N(1)-C(10)	113.2 (4)
C(6)-Ru-N(2)	86.2 (3)	Ru-N(1)-C(15)	127.4 (4)
N(1)-Ru-N(2)	71.2 (2)	Fe-N(1)-C(10)	68.9 (4)
C(7)-Fe-C(10)	130.2 (3)	Fe-N(1)-C(15)	124.5 (4)
C(7)-Fe-C(11)	130.0 (3)	C(10)-N(1)-C(15)	113.0 (6)
C(7)-Fe-N(1)	91.1 (3)	Ru-N(2)-Fe	94.2 (3)
C(7)-Fe-N(2)	91.3 (3)	Ru-N(2)-C(11)	112.2 (4)
C(10)-Fe-C(11)	39.2 (3)	Ru-N(2)-C(12)	127.8 (4)
C(10)-Fe-N(1)	40.4 (2)	Fe-N(2)-C(11)	68.8 (4)
C(10)-Fe-N(2)	69.3 (3)	Fe-N(2)-C(12)	123.5 (4)
C(11)-Fe-N(1)	69.0 (3)	C(11)-N(2)-C(12)	114.4 (6)
C(11)-Fe-N(2)	40.1 (2)		

(CO)$_4$(i-Pr-DAB)(μ_2-CO) Casarin et al. made it clear that one has to be careful using qualitative methods (as is the 18e rule) in predicting the structure of and the bonding within complexes where strong back-bonding interactions are involved.[18] This can be illustrated with the fact that in Ru$_2$(CO)$_4$(i-Pr-DAB)(μ_2-HC≡CH), where the 18e rule predicts the presence of a metal–metal bond, the results of ab initio calculations in combination with UV–PES measurements show that no bonding Ru–Ru interaction is present. Instead there are strong back-bonding interactions from the metal atoms to the bridging DAB and ethyne ligands. This study also showed that the LUMO of this type of complexes is strongly metal–metal antibonding in nature.

This explains that when this LUMO is filled, e.g. by adding a CO ligand to the Ru in FeRu(CO)$_4$(i-Pr-DAB)(μ_2-MP) (10) which is isostructural to Ru$_2$(CO)$_4$(i-Pr-DAB)(μ_2-HC≡CH), a strong antibonding Fe···Ru interaction is established, resulting in a long Fe···Ru distance.

(18) Casarin, M.; Vittadini, A.; Vrieze, K.; Muller, F.; Granozzi, G.; Bertoncello, R. *J. Am. Chem. Soc.* **1988**, 110, 1775.

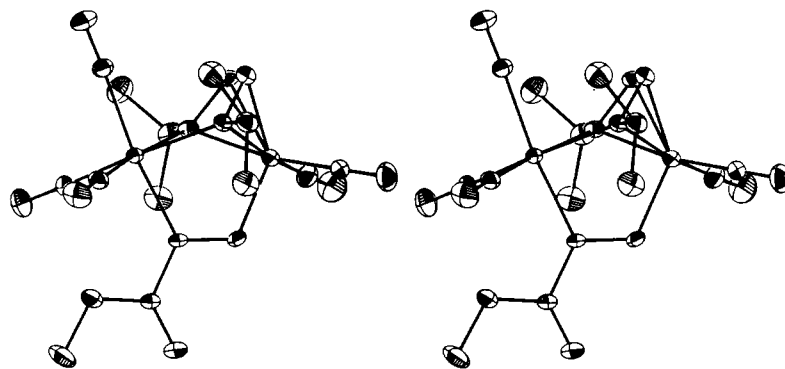**Figure 4.** Stereoscopic ORTEP representation of FeRu(CO)$_5$(*i*-Pr-DAB)(μ_2-HC≡CC(O)OMe) (8). Ellipsoid probability scale: 30%.

When at the same time the Fe-DAB and Ru-DAB distances remain roughly invariant, the only way to enlarge the Fe⋯Ru distance is to push the Ru out of the plane of the metallacycle.

The redistribution of the formal excess of electron density on the 19e Ru center proceeds via back-donation into the bridging alkyne. The elongation of the N(1)-C(11) and N(2)-C(10) bond lengths [1.402 (7) and 1.411 (7) Å, respectively] and the short central C-C bond of 1.363 (8) Å indicate that also back-donation occurs from Ru into an antibonding MO of the DAB skeleton.

NMR Spectroscopy. The ^{1}H and ^{13}C NMR data of 2 and 3 may very well be compared to those of their Fe$_2$ analogues.[2,15] Those for 4 in solution are in agreement with its molecular structure in the solid state and are comparable with those of Ru$_2$(CO)$_5$AIB(*i*-Pr,C(O)OMe,C(O)-OMe).[16] Remarkable is the very low field chemical shift of the alkyne C(15) atom at 212.4 ppm, which is about 30 ppm downfield relative to the corresponding C atom in the isostructural diruthenium complexes, which are generally observed between 170 and 185 ppm.[19] This has probably again to be related with the different bonding of the AIB ligand in the heterodinuclear complex, when compared to its diruthenium analogues (vide supra).

The ^{1}H NMR resonances for the 8e donating DAB ligands in 8–11 show the normal values for this bonding mode.[7a] The ^{1}H NMR spectrum of a mixture of 10 and 11 shows to alkyne H resonances with relative intensities 3:1 at 9.32 and 10.39 ppm. The downfield resonance is assigned to the complex 11 with the CH alkyne moiety bonded to Ru, which has a larger electron density and has also two hard σ-N donor ligands and thus causes a paramagnetic deshielding of the proton on the C atom to which it is bonded. The resonance at 9.32 ppm is thus assigned to 10, with the CH moiety bonded to Fe. The alkyne CH region of the ^{1}H NMR spectrum of complexes 8 and 9 show some dramatic shifts with respect to 10 and 11. The resonance of the alkyne CH proton at 10.39 ppm in 11 shows a considerable upfield shift to 9.95 ppm in 9. This may be rationalized with the earlier mentioned 19e (Ru)-17e (Fe) configuration of complexes 8 and 9. The redistribution of the excess of electron density from Ru to the alkyne causes a strong diamagnetic shielding of the CH fragment and thus an upfield shift. At the same time the resonance of the alkyne CH proton in 10 at 9.32 ppm shows a large downfield shift to 11.87 ppm in 8, which can be related to the deshielding effect of the electrondeficient 17e Fe center. For the OMe resonances the reverse trend is observed, i.e. a small downfield shift going from 11 to 9 and a small upfield shift going from 10 to 8.

In the ^{13}C spectra of 8 and 10 the resonances due to the DAB ligand are not very different and are found in the ranges normally observed for this coordination mode.[4] The alkyne C atoms in 8 are found at 166.0 and 200.1 ppm for the CR and CH fragments, respectively. The corresponding C atoms in 10 resonate at 137.0 and 136.4 ppm, respectively. The large downfield shifts going from 10 to 8 are probably caused by the back-donation of electron density of the 19e Ru center in 8 into a π-character MO of the bridging alkyne causing a paramagnetic deshielding of the C atoms. The shift of the other alkyne C atom is smaller because of the presence of the methoxycarbonyl substituent.

The observed ^{1}H NMR chemical shifts for 15 are in accordance with the proposed molecular structure. The ethyne protons appear as an AB pattern. The chemical shifts of 3.85 and 4.13 ppm, respectively, are normal for π-bonded olefinic fragments. The same holds for the ^{13}C chemical shifts of the corresponding C atoms of 47.8 and 51.4 ppm. The resonance at 214.6 ppm is assigned to the C atom of the CO fragment between one of the metal centers and the alkyne. The high field shift of the proton on the former imine group at 1.88 ppm is comparable to that in the complexes Fe$_2$(CO)$_5$(*i*-PrN=CHCHN(*i*-Pr)C-(O)CR=CC(O)OMe) (R = H, C(O)OMe).[2,15]

The ethyne protons in 14 and 12 give rise to a multiplet which is normally observed for metallacyclopentadienyl systems derived from ethyne. In the case of 13 a broad singlet was observed for the ethyne protons, which is probably due to the very small difference in chemical shift of the protons on the terminal and central C atoms of the butadiendiyl fragment. The small difference of the ^{13}C resonances of the terminal and central butadiendiyl C atoms of 14 suggests that the complex is structurally analogous to the diiron complex Fe$_2$[MeOC(O)C=CHCH=CC(O)OMe](CO)$_4$(*i*-Pr-DAB), in which the DAB ligand is chelating the Fe bonded to the FeC$_4$ ferracycle, for which similar ^{13}C chemical shifts are found.[20] Since the ^{13}C resonances of the CO groups bonded to Fe generally resonate at lower field when compared to CO ligands on Ru and the M(CO)$_3$ ^{13}C CO resonances appear around 197 ppm as compared to the resonance of the M(CO) fragment at 227.9 ppm, we conclude that Ru is in the MC$_4$ metallacycle and the Fe(DAB) fragment is π,π-bonded to this metallacycle (see Scheme III). The ^{13}C resonances of 12 and 13 are comparable to those of the diiron complex Fe$_2$[HC=CHCH=CH](CO)$_4$(*i*-Pr-DAB), which corroborates our structural proposal as shown in Scheme III. Both complexes differ with respect to the relative positions of Fe and Ru.

(19) Part 9 of this series: Muller, F.; van Koten, G.; Vrieze, K.; Heijdenrijk, D.; Rotteveel, M. A.; Stam, C. H.; Zoutberg, M. C. *Organometallics*, in press.

(20) 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.

Complex Formation. An intriguing aspect of the reaction of 1 with DMADC is the formation of one product, 2, with both N atoms bonded to Ru and a second product, 4, with both N atoms bonded to Fe, which is also the case in FeRu(CO)$_6$(*i*-Pr-DAB) (1). This product distribution may satisfactorily be explained by assuming the occurrence of a reversible isomerization process from 1 to 1' involving the migration of the η^2-C=N bonded imine fragment from Fe to Ru and vice versa (see Scheme I). Such a process is analogous to the reversible (photo)isomerization processes of complexes Fe$_2$(CO)$_5$(R-DAB)(PR'$_3$), reported by Frühauf et al.[21] The thermodynamically stable isomer of 1, of which also the X-ray crystal structure was established,[6] with the η^2-C=N imine fragment bonded to Fe, thus reacts via the substitution of this imine fragment by a DMADC molecule and the subsequent loss of CO to give 2 with both N atoms bonded to Ru. This reaction is analogous to that of the homodinuclear complex Fe$_2$-(CO)$_6$(*i*-Pr-DAB) with DMADC.[2] The second isomer 1' which cannot be isolated or observed reacts via a direct electrophilic attack of the DMADC ön the coordinated imine C atom and the subsequent loss of a CO group to give the C–C coupling product 4 in a reaction analogous to that of the diruthenium complex Ru$_2$(CO)$_6$(*i*-Pr-DAB) with DMADC.[16,19] This suggests that the nature of the η^2-C=NM interaction plays an important role in the product distribution of the reactions of M$_2$(CO)$_6$(L) [M$_2$ = Fe$_2$, Ru$_2$, FeRu; L = R-DAB, R-Pyca] with alkynes. The observations that under UV irradiation only 4 can be isolated and that under exclusion of light the relative yield of 2 with respect to 4 is strongly enhanced are completely supportive of these mechanisms, since the above-mentioned analogous isomerization of Fe$_2$(CO)$_5$(R-DAB)(PR'$_3$) is photochemically induced.[21] The relatively high yield of 4 and the fact that the isomerization product 1' has as yet never been isolated or even spectroscopically observed seem to be in contradiction. We therefore have to assume that the reaction of 1' with DMADC to give 4 is significantly faster than the reaction of 1 to give 2. Although the equilibrium between 1 and 1' lies strongly at the side of 1, this difference in relative reaction rates may explain the high yield of 4.

The thermally induced rearrangement of 2 to 3 most likely involves a mechanism comparable to that of the diiron analogue comprising the direct transfer of the methine H atom to the coordinated alkyne, without involving a metal–hydride intermediate.[2] It must be noted, however, that only one isomer of 3 is formed, whereas in the case of the diiron analogue two isomeric complexes resulting from the migration of an H atom from an isopropyl methine group to the alkyne are observed.

The question why 1 reacts with DMADC to give the substitution of the η^2-C=N bonded imine fragment, while 1' leads to a C–C coupling product, is difficult to answer. This question is related to that of why only 1, with the η^2-C=N imine fragment bonded to Fe, can be isolated or observed. An important aspect is obviously the relative strengths of the η^2-C=NFe and η^2-C=NRu interactions. The fact that η^2-C=N coordination to Ru leads to C–C coupling suggests a stronger back-bonding which leads on the one hand to a weaker C–N bond and on the other hand to an enhanced nucleofilicity of the imine C atom. These effects result in an activation of this imine fragment toward an electrophilic attack of the alkyne. The relatively weaker η^2-C=NFe bonding results in an easy substitution, e.g. by an alkyne. This rationale, however, seemingly

contradicts the above-mentioned preference for the η^2-C=N bonding to Fe in 1. A possible explanation is that a stronger η^2-C=N coordination to Fe also means that the η^2-C=C coordination in the substitution product is more stable to Fe than to Ru, and Ru thus prefers the C–C coupling reaction path.

The reaction of 1 with methyl propynoate apparently does not involve an isomerization of the starting complex 1, since only products with the N atoms σ-bonded to Ru are observed. Although complexes 10 and 11 and also 8 and 9 are structurally closely related to their homonuclear analogues Ru$_2$(CO)$_4$(*i*-Pr-DAB)(μ_2-HC≡CH) and Fe$_2$-(CO)$_4$(*i*-Pr-DAB)(μ_2-HC≡CC(O)OMe), we propose that their formation proceeds via a different mechanism. The formation of the latter two complexes from M$_2$(CO)$_6$(R-DAB) with alkynes most likely proceeds via the initial loss of one CO ligand to give M$_2$(CO)$_5$(R-DAB), of which subsequently the bridging CO ligand is substituted by the alkyne.[14] This has been demonstrated by the fact that when M = Ru, the intermediate Ru$_2$(CO)$_5$(R-DAB) can be isolated and indeed reacts with ethyne to give Ru$_2$(CO)$_4$-(*i*-Pr-DAB)(μ_2-HC≡CH). In the case of Fe, Fe$_2$(CO)$_4$(*i*-Pr-DAB)(μ_2-HC≡CC(O)OMe) is only formed when the reaction mixture of Fe$_2$(CO)$_6$(*i*-Pr-DAB) and MP is purged with N$_2$, thus generating the unstable intermediate Fe$_2$-(CO)$_5$(*i*-Pr-DAB) which reacts with the alkyne.

There is, however, no reason to assume the initial formation of FeRu(CO)$_5$(*i*-Pr-DAB) (5) when 1 is stirred at 20 °C in a hexane solution in the presence of MP since, despite considerable efforts, such a complex has as yet never been isolated or observed.[6] The reaction of 1 with ethyne at 98 °C in refluxing heptane to give 6 probably does proceed via 5. The formation of this intermediate (5) is enhanced by the combination of the high temperature (at 90 °C no formation of 6 is observed) and the passing of a gas (ethyne) through the reaction mixture. FeRu(CO)$_5$(*i*-Pr-DAB) can also be generated when 1 is reacted with Me$_3$NO and in the presence of DMADC reacts to give FeRu(CO)$_4$(*i*-Pr-DAB)(μ_2-DMADC), although in very low yield (see Scheme II).[6] We are therefore inclined to assume that another mechanism is involved in the reaction of 1 with MP. The most realistic proposal for an alternative mechanism is the initial insertion of the MP in the Fe–Ru bond in 1 to give 7, after which one of the CO ligands on Fe is substituted by a second η^2-C=N coordination, giving 8, 9 (see Scheme II). The observation (see Experimental Section) that the irradiation of the reaction mixture leads to a slight decrease of the reaction rate supports our view that 1' does not react with MP and therefore the 1–1' isomerization process plays no role in this reaction.

The reversible conversion of 8, 9 into 10, 11 is reminiscent of an analogous reversible CO addition, i.e. in the reaction of Ru$_3$(CO)$_8$(R-DAB(8e)) with CO to give Ru$_3$-(CO)$_9$(R-DAB(8e)). Also in these complexes there is an 8e donating R-DAB ligand and CO addition/elimination takes place on the Ru in the RuN$_2$C$_2$ metallacycle.[22] Ru$_3$(CO)$_8$(R-DAB(8e)) is a normal 48e cluster, while Ru$_3$(CO)$_9$(R-DAB(8e)) is a 50e cluster. The two electrons introduced by the incoming CO ligand do not lead to the fission of a metal–metal bond, as in 8, 9, but are delocalized over two Ru–Ru bonds which show a significant elongation but remain intact. The crystal structures of the isostructural diiron[14] and diruthenium[17] complexes suggest that, as in Ru$_3$(CO)$_8$(R-DAB(8e)), in 10 and 11 there is an empty coordination site on the Ru in the RuN$_2$C$_2$ metal-

(21) Frühauf, H.-W.; Meyer, D.; Breuer, J. *J. Organomet. Chem.* **1985,** *297*, 211.

(22) Keijsper, J.; Polm, L. H.; van Koten, G.; Vrieze, K.; Seignette, P. F. A. B.; Stam, C. H. *Inorg. Chem.* **1985,** *24*, 518.

lacycle where the incoming CO can easily attack.

The formation of complexes 12–14 with the DAB chelating different metal centers in the reaction of 1 with ethyne suggests that also in this reaction the isomerization of 1 plays an important role. It seems not unlikely that the reactions of ethyne with 1 and 1′ to give 12–14 involves a mechanism comparable to that of the formation of the analogous diiron ferracyclopentadienyl complexes.[20] It has been shown that the formation of $Fe_2[C_4(C(O)OMe)_4]$-$(CO)_4(i\text{-Pr-DAB})$ involves an intermediate complex Fe_2-$(CO)_5(i\text{-Pr-DAB})(\mu_2,\eta^2\text{-DMADC})$ with a chelating DAB ligand and a perpendicular bridging alkyne, as in 2. In a similar fashion 1 and 1′ react with ethyne via a substitution of the $\eta^2\text{-C}{=}N$ bonded imine by an $\eta^2\text{-C}{\equiv}C$ bonded ethyne molecule. Via the elimination of one CO an intermediate of type 2 is formed which reacts with a second ethyne molecule to give 12–14 (see Scheme III). The only other known examples of heterodinuclear FeRu metallacyclopentadienyl complexes have been reported by Nakamura et al., although their formation proceeds via an entirely different mechanism.[23]

When we compare the reactivity of 1 toward alkynes with that of its homodinuclear Fe and Ru parent compounds, we can generally conclude that the product distribution shows features of both of those of the Fe_2 and the Ru_2 complexes. The flyover and metallacyclopentadienyl complexes 12–15 may be compared with products of $Fe_2(CO)_6(R\text{-DAB})$, while the complexes like 4 have until now only been found in the Ru_2 chemistry. Complexes with an 8e donating R-DAB ligand and a μ_2-bridging alkyne like in 6 and 8–11 are known for the Fe_2 as well as for the Ru_2 chemistry.

When we relate the facts that the most stable isomer of 1 has the $\eta^2\text{-C}{=}N$ imine fragment bonded to Fe and that the majority of the products of 1 with alkynes is analogous to Fe_2 product types, it becomes clear that the nature of the $\eta^2\text{-C}{=}NM$ interaction of the σ-N, $\mu_2\text{-N}′$, $\eta^2\text{-C}{=}N′$ bonded α-diimine ligand is a major factor influencing the course of the reactions of $M_2(CO)_6(\alpha\text{-diimine})$ with alkynes. This is probably also the reason that the present results on the chemical behavior of $FeRu(CO)_6(i\text{-Pr-DAB})$ differ from that of the heterodinuclear complex $(Cp)_2FeRu(CO)_4$.

From a study of the chemistry of this complex, Knox et al. have concluded that its chemical behavior closely resembles that of its diiron analogue and that at the same time it is more reactive than both its homodinuclear parent compounds.[24]

Conclusions

The results of the reactions of 1 with alkynes have provided a number of valuable insights in the chemistry of dinuclear metal carbonyl α-diimine complexes with alkynes. The nature of the AIB complex 4 shows that the ligands which are formed in the reactions of complexes $M_2(CO)_6(\alpha\text{-diimine})$ with alkynes can adjust to the different electron distribution in the heterobimetallic FeRu complex, when compared to the homodinuclear analogues, by slightly changing their coordination mode. It has further become clear that in the reaction of $M_2(CO)_6(L)$ complexes with alkynes we have to consider the possibility of the migration of the α-diimine from one metal center to the other. The most important conclusion is that the product distribution of the reactions is strongly influenced by the nature of the $\eta^2\text{-C}{=}NM$ interaction.

Supplementary Material Available: A table of the anisotropic thermal parameters of the non-H atoms, a table of the calculated fractional coordinates of the H atoms, and a full listing of bond lengths and angles of the non-H atoms for 4 and a table of the anisotropic thermal parameters of the non-H atoms, a table of fractional coordinates of the H atoms, a listing of bond lengths and angles of the H atoms, and a full listing of the bond lengths and angles of the non-H atoms for 8 (10 pages); listings of observed and calculated structure factors for 4 and 8 (47 pages). Ordering information is given on any current masthead page.

(23) Noda, I.; Yasuda, H.; Nakamura, A. *J. Organomet. Chem.* **1983**, *250*, 447.

(24) Gracey, B. P.; Knox, S. A. R.; Macpherson, K. A.; Orpen, A. G.; Stobart, S. R. *J. Chem. Soc., Dalton Trans.* **1985**, 1935.