

Synthesis of some Dinuclear Fe and Ru Complexes Containing an 8e Donating α -Diimine Ligand and a μ_2 -Bridging Alkyne; Crystal Structure of $(\sigma, \sigma\text{-}N, N', \eta^2, \eta^2\text{-C=N, C=N}'\text{-}1, 4\text{-Diisopropyl-}1, 4\text{-diaz-}1, 3\text{-butadiene})(\mu_2\text{-methyl propynoate})$ Tetracarbonyl Di-iron*

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Abstract

Reaction of $\text{Fe}_2(\text{CO})_6(\text{i-Pr-DAB})$ [i-Pr-DAB = i-Pr-N=C(H)C(H)=N-i-Pr] with methyl propynoate at room temperature in heptane solution, through which a stream of nitrogen is passed, yields the complex $\text{Fe}_2(\text{CO})_4(\text{i-Pr-DAB})(\mu_2\text{-HC}\equiv\text{CC}(\text{O})\text{OMe})$ among a number of other products. The α -diimine ligand is $\sigma, \sigma\text{-}N, N', \eta^2, \eta^2\text{-C=N, C=N}'$ coordinated, thus donating eight electrons to the metal carbonyl core. This compound, of which the structure is confirmed by an X-ray crystal structure determination, is the first Fe complex with an R-DAB ligand in this coordination mode.

Crystals of $\text{Fe}_2\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_6 \cdot 0.15\text{C}_6\text{H}_6$ are monoclinic, space group $A2/a$, and have cell constants $a = 31.450(6)$, $b = 9.602(3)$, $c = 28.191(6)$ Å, $\beta = 91.606(19)^\circ$ and $Z = 16$. 3017 reflections (Mo $K\alpha$, $\mu = 13.9 \text{ cm}^{-1}$) have been used in the refinement resulting in a final R value of 0.056.

In the compound, which is structurally analogous to the previously reported $\text{Ru}_2(\text{CO})_4(\text{i-Pr-DAB})(\mu_2\text{-HC}\equiv\text{CH})$, the alkyne is in a bridging position along the metal–metal bond [Fe(11)–C(15): 1.924(8); Fe(12)–C(16): 2.007(7) Å]. The Fe–Fe distance of 2.670(4) Å is normal for a single Fe–Fe bond. The carbonyl ligands are all terminally bonded, two to either Fe atom, with normal bond lengths and angles. The Fe atoms and the non-H atoms of the coordinated alkyne lie in one plane, which is also a plane of symmetry in the molecule. The bond distances within the DAB ligand and between the ligand and the Fe atoms are as expected for the $\sigma, \sigma\text{-}N, N', \eta^2, \eta^2\text{-C=N, C=N}'$ coordination mode.

Reaction of $\text{Ru}_2(\text{CO})_6(\text{i-Pr-DAB})$ with phenylacetylene in heptane solution at 90°C , yields two isomeric compounds $\text{Ru}_2(\text{CO})_4(\text{i-Pr-DAB})(\mu_2\text{-PhC}\equiv\text{CH})$, which have a molecular structure comparable to that of $\text{Fe}_2(\text{CO})_4(\text{i-Pr-DAB})(\mu_2\text{-HC}\equiv\text{CC}(\text{O})\text{OMe})$.

The formation of the alkyne complexes from $\text{M}_2(\text{CO})_6(\text{i-Pr-DAB})$ [M = Fe, Ru] probably proceeds via $\text{M}_2(\text{CO})_5(\text{i-Pr-DAB})$ [M = Fe, Ru], through the loss of one CO with concomitant change of coordination of the i-Pr-DAB from the 6e to the 8e donating mode. Substitution of a second CO by an alkyne yields $\text{M}_2(\text{CO})_4(\text{i-Pr-DAB})(\mu_2\text{-RC}\equiv\text{CH})$ [M = Fe, R = C(O)OMe; M = Ru, R = H, Ph]. This indicates that $\text{Fe}_2(\text{CO})_5(\text{i-Pr-DAB})$, which until now never has been observed or isolated, is a likely intermediate in reactions of $\text{Fe}_2(\text{CO})_6(\text{i-Pr-DAB})$.

Introduction

The reactivity of the α -diimine ligand R-DAB [R-DAB = 1,4-DiAza-1,3-Butadiene; $\text{RN}=\text{C}(\text{H})\text{C}(\text{H})=\text{NR}$] towards metal carbonyl clusters of the iron triad has been studied extensively [1a–d]. One of the interesting aspects of this study is the very versatile coordination behaviour of the R-DAB ligand, which can donate from four up to eight electrons to the metal carbonyl core to which it is bonded. The 4e donating [2, 3][†] (via the nitrogen lone pairs) and the 6e donating [4] (via the nitrogen lone pairs and one of the C=N bonds) coordination modes have been found in Fe as well as Ru and Os complexes. The 8e donating coordination mode, in which the ligand donates four electrons via the nitrogen lone

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[†]Mononuclear $\text{Fe}(\text{CO})_3(\text{R-DAB})$ complexes with an $\eta^2, \eta^2\text{-C=N, C=N}'$ coordinated R-DAB ligand have been observed in a matrix at 10 K after photolysis of $\text{Fe}(\text{CO})_3(\sigma, \sigma\text{-}N, N'\text{-R-DAB})$ [2].

pairs and four electrons via the two C=N π -bonds, however, has until now only been observed in Ru and Os complexes [5–11].

The first example of a Ru complex containing an 8e donating R-DAB ligand was reported by us some years ago [8]. This complex, $\text{Ru}_2(\text{CO})_4(\text{i-Pr-DAB})(\mu_2\text{-HC}\equiv\text{CH})$ (**3b**), resulted from the reaction of $\text{Ru}_2(\text{CO})_6(\text{i-Pr-DAB})$ with acetylene. Also other reactions of $\text{Ru}_2(\text{CO})_6(\text{R-DAB})$ with alkynes were studied, producing a number of novel and interesting organometallic complexes [12].

We therefore extended this study to the reactivity of the analogous Fe complexes towards alkynes. We now report the synthesis and X-ray crystal structure of the complex $\text{Fe}_2(\text{CO})_4(\text{i-Pr-DAB})(\mu_2\text{-HC}\equiv\text{CC}(\text{O})\text{-OMe})$ (**3a**), which is formed in the reaction of $\text{Fe}_2(\text{CO})_6(\text{i-Pr-DAB})$ with methyl propynoate among a number of other products and which is the first example of an Fe complex with an 8e donating R-DAB ligand. From the reaction of $\text{Ru}_2(\text{CO})_6(\text{i-Pr-DAB})$ with phenylacetylene at 90 °C, we isolated two isomeric complexes $\text{Ru}_2(\text{CO})_4(\text{i-Pr-DAB})(\mu_2\text{-PhC}\equiv\text{CH})$ (**3c, d**). The complexes **3a**, **3c** and **3d** are structurally analogous to **3b**, of which the formation is now better understood.

Experimental

Materials and Apparatus

^1H NMR spectra were obtained on a Bruker AC100 spectrometer. ^{13}C NMR spectra were recorded on Bruker AC100 and WM250 spectrometers. Chemical shifts are reported in ppm relative to Me_4Si . IR spectra were recorded on a Perkin-Elmer 283 spectrometer. FD-mass spectra were measured 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. Fast Atom Bombardment (FAB) mass spectrometry was carried out using a VG Micromass ZAB-2F mass spectrometer, an instrument with reverse geometry and fitted with a high field magnet and coupled to a VG 11-250 data system. The samples were loaded in diethanolamine onto a stainless steel probe and bombarded with Xenon-atoms having 8 keV energy. During the high resolution FAB-MS measurements a resolving power of 25 000 (10% valley definition) was used. 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 using silicagel (60 Mesh, dried and activated before use) as the stationary phase. i-Pr-DAB and $\text{Fe}_2(\text{CO})_6(\text{i-Pr-DAB})$ were prepared according to known

procedures [13]. Methyl propynoate, phenylacetylene and $\text{Ru}_3(\text{CO})_{12}$ were used as commercially obtained.

Synthesis of $\text{Fe}_2(\text{CO})_4(\text{i-Pr-DAB})(\mu_2\text{-HC}\equiv\text{CC}(\text{O})\text{-OMe})$ (**3a**)

$\text{Fe}_2(\text{CO})_6(\text{i-Pr-DAB})$ (**1a**) (2 mmol, 840 mg) and methyl propynoate (4 mmol, 336 mg) were dissolved in 50 ml of heptane. At 20 °C and with stirring, nitrogen was bubbled through the solution through a gas inlet tube. After 24 h the solvent and the excess of alkyne were evaporated. The crude reaction mixture was extracted with diethyl ether. The ether was evaporated and the product mixture was separated by column chromatography. Small amounts of $\text{Fe}(\text{CO})_3(\text{i-Pr-DAB})$ and unreacted **1a** were obtained using hexane and hexane/diethyl ether (9:1) respectively as eluents. Elution with hexane/diethyl ether (3:1) produced a solution of the orange–red **3a** (yield 15–20%), which was identified by elemental analysis, IR, FD-mass, ^1H and ^{13}C NMR spectroscopy and by an X-ray crystal structure. Further elution with hexane/diethyl ether (7:3) and hexane/diethyl ether (1:1) provided three more compounds all with the general formula $\text{Fe}_2(\text{CO})_6(\text{i-Pr-DAB})(\text{HC}\equiv\text{CC}(\text{O})\text{OMe})^*$.

Crystals of **3a** suitable for X-ray crystallography were obtained by recrystallization from a hexane/diethyl ether solution at –30 °C. Recrystallization, however, could not prevent the inclusion of benzene in the crystal (about 0.3 molecules per asymmetric unit), probably originating from traces of benzene in the system in which the synthesis was carried out (rubber tubes etc.). The compound analyzed as: C, 42.92 (42.89); H, 4.67 (4.50); N, 5.82 (6.25)% (values calculated for $\text{Fe}_2\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_6$ in parentheses). FD-mass: $M = 448$ (calculated: $M = 448.04$). IR [$\nu(\text{CO})$, hexane solution, cm^{-1}]: 2024(m), 1995(s), 1974(s), 1938(s), 1715(w).

Synthesis of $\text{Ru}_2(\text{CO})_4(\text{i-Pr-DAB})(\mu_2\text{-PhC}\equiv\text{CH})$ (**3c, d**)

$\text{Ru}_3(\text{CO})_{12}$ (1 mmol, 639 mg) and i-Pr-DAB (1.8 mmol, 250 mg) were stirred in 50 ml of heptane for 30 min at 80 °C. The obtained dark red solution was refluxed for 2 h. After cooling to room temperature the unreacted $\text{Ru}_3(\text{CO})_{12}$ was filtered off and phenylacetylene (2.5 mmol, 255 mg) was added to the orange–red solution of $\text{Ru}_2(\text{CO})_6(\text{i-Pr-DAB})$ (**1b**) [13]. The mixture was heated to 90 °C. After about half an hour, when in the IR spectrum the bands of the starting complex (**1b**) had disappeared, the reaction was stopped and the obtained brown solution was evaporated to dryness. The crude reaction mixture was separated by column chromato-

*These compounds will be discussed in forthcoming parts of this series [14].

graphy. A 2:1 mixture of **3c** and **3d** was obtained by elution with hexane/diethyl ether (9:1) as a dark yellow fraction in about 50% yield. FAB-MS exact mass determination (based on ^{102}Ru): $M = 557.9670$ (calculated: $M = 556.54$). IR [$\nu(\text{CO})$, hexane solution, cm^{-1}]: 2025(m), 2005(s), 1959(s), 1945(s). Attempts to separate both isomers by further chromatography or crystallization were not successful.

Crystal Structure Determination of $\text{Fe}_2(\text{CO})_4(\text{i-Pr-DAB})(\mu_2\text{-HC}\equiv\text{CC}(\text{O})\text{OMe})$ (**3a**)

The dark red crystals of **3a** ($\text{Fe}_2\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_6 \cdot 0.15\text{C}_6\text{H}_6$, $M(\text{Fe}_2\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_6) = 448.04$) are monoclinic, space group $A2/a$ (non standard setting of $C2/c$), cell constants $a = 31.450(6)$, $b = 9.602(3)$, $c = 28.191(6)$ Å, $\beta = 91.606(19)^\circ$ and $Z = 16$, $V = 8506.5$ Å³, $D_{\text{calc}} = 1.44$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 13.9$ cm⁻¹. The crystal dimensions are $0.45 \times 0.38 \times 0.15$ mm.

8511 intensities ($2.2 < 2\theta < 40^\circ$, $-31 < h < 31$, $-1 < k < 10$, $-27 < l < 27$) were measured at 20 °C on a Nonius CAD4 diffractometer, using graphite monochromated Mo K α radiation (scan method: θ - 2θ). 5494 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 Fe atoms were located using the symbolic addition program set SIMPEL [15]. The C, N and O atomic positions were derived from an F_{obs} -Fourier synthesis. The positions of the H atoms were calculated and not refined. After anisotropic block diagonal least-squares refinement of the structure, a ΔF -Fourier synthesis showed some residual electron density, which appeared to be due to about

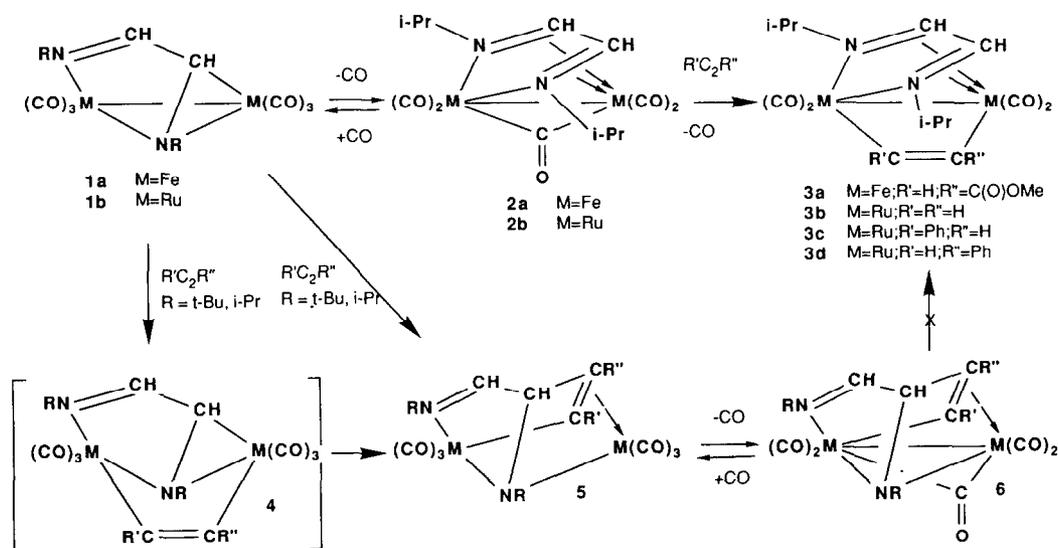
0.3 molecules of benzene per asymmetric unit. The positions of the benzene C atoms were poorly defined and were refined isotropically. The refinement converged to a final R value of 0.056 for 3017 observed reflections. Unit weights were used and no extinction or absorption correction was applied. The anomalous dispersion of Fe was taken into account. The calculations were performed with XRAY76 [16], the atomic scattering factors were taken from Cromer and Mann (1968) [17], the dispersion correction from the International Tables for X-ray Crystallography [18].

Results

$\text{Fe}_2(\text{CO})_6(\text{i-Pr-DAB})$ [$\text{i-Pr-DAB} = \text{i-Pr-N}=\text{C}(\text{H})\text{C}(\text{H})=\text{N-i-Pr}$] (**1a**) reacts with methyl propynoate at 20 °C in a heptane solution, which is purged with nitrogen, to give a mixture of products of which $\text{Fe}_2(\text{CO})_4(\text{i-Pr-DAB})(\mu_2\text{-HC}\equiv\text{CC}(\text{O})\text{OMe})$ (**3a**) is discussed in this paper. $\text{Ru}_2(\text{CO})_6(\text{i-Pr-DAB})$ (**1b**) reacts with phenylacetylene at 90 °C in heptane solution to give **3c** and **3d**, both with the formula $\text{Ru}_2(\text{CO})_4(\text{i-Pr-DAB})(\mu_2\text{-PhC}\equiv\text{CH})$, in a 2:1 ratio. These latter complexes only differ in the way the alkyne is bonded to the metal carbonyl core. In **3c** the CPh moiety of the alkyne is bonded to the Ru atom to which both DAB N atoms are σ -bonded, whereas in **3d** the CH moiety of the alkyne is bonded to this Ru atom. These reactions are shown in Scheme 1.

Molecular Structure of **3a**

In the crystal structure of **3a**, the asymmetric unit contains two independent molecules 1 and 2,



Scheme 1. Formation of $\text{M}_2(\text{CO})_4(\text{R-DAB})(\mu_2\text{-R}'\text{C}\equiv\text{CH})$ [$\text{M} = \text{Fe}, \text{Ru}$; $\text{R} = \text{i-Pr}$].

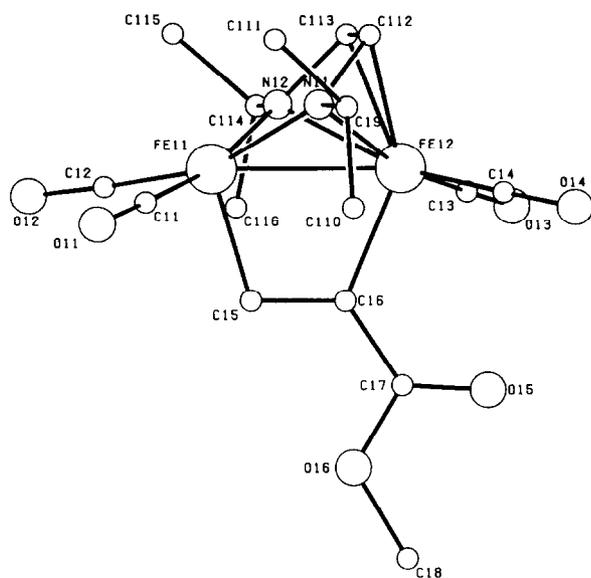


Fig. 1. PLUTO drawing of molecule 1 of **3a**. The H atoms are omitted for clarity.

which are identical in molecular geometry and differ only slightly in bond lengths and angles. In the following discussion of the molecular geometry of **3a**, the bond lengths and angles of molecule 1 are used. The molecular geometry of molecule 1 and the adopted atomic numbering are shown in Fig. 1. Figure 2 shows an ORTEP stereoscopic view of the same molecule. The positional parameters of both molecules are listed in Table 1. The bond lengths and angles are listed in Tables 2 and 3.

The molecular structure of **3a** can be described as consisting of an $\text{Fe}_2(\text{CO})_4$ core with four terminal COs and a single Fe–Fe bond [Fe(11)–Fe(12): 2.670(4) Å]. The Fe–Fe bond is bridged by the *i*-Pr-DAB ligand and by the methyl propynoate molecule. The *i*-Pr-DAB ligand is coordinated in the

8e donating coordinating mode, which makes this compound the first example of an Fe complex with an R-DAB ligand bonded in this mode. The two N atoms coordinate to Fe(11) [Fe(11)–N(11): 1.964(7), Fe(11)–N(12): 1.968(7) Å] via their lone pairs, thus donating four electrons. Both C=N imine bonds coordinate via their π -electrons to Fe(12), also donating four electrons [Fe(12)–N(11): 2.106(7); Fe(12)–N(12): 2.094(8); Fe(12)–C(112): 2.045(8); Fe(12)–C(113): 2.039(9) Å]. The bond lengths within the DAB ligand [N(11)–C(112): 1.385(11); C(112)–C(113): 1.347(12); C(113)–N(12): 1.393(10) Å] and those between the metal atoms and the DAB ligand are comparable to those in other complexes with the R-DAB ligand coordinated in the 8e donating mode [5–11, 19]. The methyl propynoate molecule is bonded to the complex along the Fe–Fe bond via two σ -Fe–C bonds [Fe(11)–C(15): 1.924(8); Fe(12)–C(16): 2.007(7) Å]. The C(15)–C(16) bond length of 1.306(11) Å and the bond angles around C(15) and C(16) indicate a reduction of the former alkyne bond to an olefinic bond, combined with a change in hybridization of C(15) and C(16) from sp to sp^2 .

The structural features of the Fe complex reported here strongly resemble those of the complex $\text{Ru}_2(\text{CO})_4(\textit{i}\text{-Pr-DAB})(\mu_2\text{-HC}\equiv\text{CH})$ (**3b**), reported by us some years ago [8], which was then the first example of an 8e donating R-DAB ligand. Apart from the expected differences between the Fe and Ru complexes with respect to the metal–metal and metal–ligand bond lengths, the C(15)–C(16) bond distance of 1.306(11) Å in the Fe complex is somewhat shorter than the corresponding C–C bond length of 1.342(12) Å in the Ru complex. For dinuclear complexes with an alkyne bridging along the metal–metal bond, C–C bond lengths in the range of 1.25–1.40 Å are normally observed [20–23]. There is, however, no distinct relation between

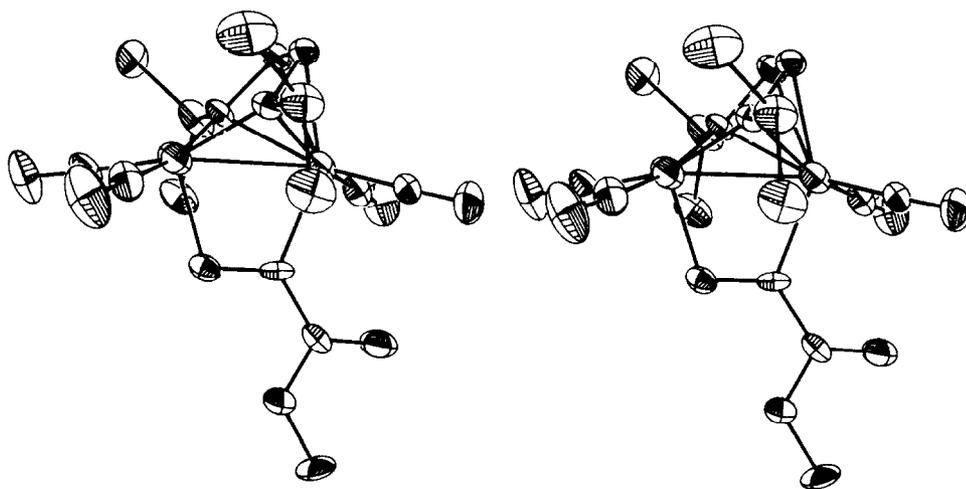


Fig. 2. Stereoscopic ORTEP representation of molecule 1 of **3a** (ellipsoid probability scale: 30%).

TABLE 1. Fractional Coordinates and Equivalent Isotropic Thermal Parameters of the Non-hydrogen Atoms of 3a

Atom	x	y	z	U_{eq}
Fe(11)	0.36605(5)	0.48086(18)	0.36752(5)	0.0592(10)
Fe(12)	0.30433(5)	0.31749(17)	0.39931(5)	0.0562(10)
C(11)	0.3695(4)	0.6599(14)	0.3557(4)	0.061(9)
C(12)	0.4076(4)	0.4628(13)	0.3291(4)	0.059(9)
C(13)	0.2876(4)	0.1463(13)	0.3866(4)	0.055(8)
C(14)	0.2544(4)	0.3499(12)	0.4198(4)	0.048(8)
C(15)	0.3236(4)	0.4628(11)	0.3173(4)	0.043(7)
C(16)	0.2924(3)	0.3881(11)	0.3333(3)	0.038(7)
C(17)	0.2550(4)	0.3475(13)	0.3058(4)	0.051(8)
C(18)	0.2167(5)	0.3598(18)	0.2309(4)	0.086(11)
C(19)	0.3120(4)	0.6205(14)	0.4464(4)	0.063(9)
C(110)	0.2827(5)	0.6895(15)	0.4121(5)	0.083(11)
C(111)	0.3449(6)	0.7180(17)	0.4692(5)	0.097(13)
C(112)	0.3390(3)	0.3856(13)	0.4572(4)	0.047(8)
C(113)	0.3580(4)	0.2731(13)	0.4387(4)	0.054(8)
C(114)	0.3900(4)	0.1609(13)	0.3705(4)	0.059(9)
C(115)	0.4373(4)	0.1620(16)	0.3811(5)	0.076(10)
C(116)	0.3784(5)	0.1438(14)	0.3189(4)	0.068(10)
N(11)	0.3346(3)	0.4974(10)	0.4265(3)	0.045(6)
N(12)	0.3698(3)	0.2890(10)	0.3918(3)	0.045(6)
O(11)	0.3739(4)	0.7759(10)	0.3462(4)	0.112(9)
O(12)	0.4360(3)	0.4593(12)	0.3043(4)	0.102(8)
O(13)	0.2762(3)	0.0356(9)	0.3790(3)	0.087(7)
O(14)	0.2204(3)	0.3712(11)	0.4342(3)	0.080(7)
O(15)	0.2257(3)	0.2785(12)	0.3185(3)	0.096(8)
O(16)	0.2526(3)	0.4005(10)	0.2618(3)	0.066(6)
Fe(21)	0.08034(5)	-0.10316(17)	0.32688(5)	0.0573(10)
Fe(22)	0.13115(5)	0.04573(17)	0.38578(5)	0.0571(10)
C(21)	0.0299(4)	-0.0836(12)	0.3016(4)	0.045(7)
C(22)	0.0714(4)	-0.2817(13)	0.3191(4)	0.060(9)
C(23)	0.1711(4)	0.0076(13)	0.4278(4)	0.054(8)
C(24)	0.1242(4)	0.2064(13)	0.4150(4)	0.055(8)
C(25)	0.0579(3)	-0.1138(12)	0.3905(4)	0.044(7)
C(26)	0.0842(4)	-0.0448(11)	0.4196(4)	0.044(7)
C(27)	0.0768(4)	-0.0370(13)	0.4714(4)	0.053(8)
C(28)	0.0364(5)	-0.1114(19)	0.5355(5)	0.100(13)
C(29)	0.1702(4)	-0.2356(14)	0.3482(4)	0.057(9)
C(210)	0.1526(5)	-0.3305(14)	0.3875(5)	0.072(10)
C(211)	0.1778(5)	-0.3208(16)	0.3033(5)	0.079(11)
C(212)	0.1650(3)	0.0014(13)	0.3264(4)	0.048(8)
C(213)	0.1409(3)	0.1187(12)	0.3187(4)	0.044(7)
C(214)	0.0710(4)	0.2258(12)	0.3173(4)	0.061(9)
C(215)	0.0310(4)	0.2237(14)	0.3454(5)	0.069(10)
C(216)	0.0614(5)	0.2519(14)	0.2654(4)	0.073(10)
N(21)	0.1419(3)	-0.1159(9)	0.3368(3)	0.043(6)
N(22)	0.0970(3)	0.0940(9)	0.3227(3)	0.042(6)
O(21)	-0.0035(3)	-0.0772(11)	0.2830(3)	0.077(7)
O(22)	0.0631(3)	-0.3951(10)	0.3134(4)	0.100(8)
O(23)	0.1977(3)	-0.0131(11)	0.4558(3)	0.085(7)
O(24)	0.1206(3)	0.3110(10)	0.4331(3)	0.085(7)
O(25)	0.0977(3)	0.0328(11)	0.4980(3)	0.081(7)
O(26)	0.0460(3)	-0.1177(10)	0.4859(3)	0.080(7)

Atoms belonging to the independent molecules 1 and 2 are numbered 1... and 2... respectively.

the M–M bond lengths and the C–C bond lengths. The latter seem to depend on the M–M bond distance and the nature of the metal, as well as on electronic and steric influences of the ligands and the sub-

stituents on the alkyne. Therefore it is difficult to conclude whether the shorter C–C distance in the Fe complex is caused by the shorter Fe–Fe interatomic distance (*i.e.* 2.670(4) Å as compared

TABLE 2. Bond Distances (Å) of the Non-hydrogen Atoms of 3a^a

Fe(11)–Fe(12)	2.670(4)	Fe(21)–Fe(22)	2.684(3)
Fe(11)–C(11)	1.755(9)	Fe(21)–C(21)	1.732(8)
Fe(11)–C(12)	1.731(9)	Fe(21)–C(22)	1.750(9)
Fe(11)–C(15)	1.924(8)	Fe(21)–C(25)	1.949(8)
Fe(11)–N(11)	1.964(7)	Fe(21)–N(21)	1.951(7)
Fe(11)–N(12)	1.968(7)	Fe(21)–N(22)	1.969(6)
Fe(12)–C(13)	1.759(9)	Fe(22)–C(23)	1.742(9)
Fe(12)–C(14)	1.715(9)	Fe(22)–C(24)	1.765(9)
Fe(12)–C(16)	2.007(7)	Fe(22)–C(26)	1.981(9)
Fe(12)–C(112)	2.045(8)	Fe(22)–C(212)	2.054(8)
Fe(12)–C(113)	2.039(9)	Fe(22)–C(213)	2.048(8)
Fe(12)–N(11)	2.106(7)	Fe(22)–N(21)	2.111(6)
Fe(12)–N(12)	2.094(8)	Fe(22)–N(22)	2.103(6)
C(11)–O(11)	1.155(12)	C(21)–O(21)	1.160(10)
C(12)–O(12)	1.149(12)	C(22)–O(22)	1.130(11)
C(13)–O(13)	1.140(11)	C(23)–O(23)	1.151(11)
C(14)–O(14)	1.173(11)	C(24)–O(24)	1.134(11)
C(15)–C(16)	1.306(11)	C(25)–C(26)	1.326(11)
C(16)–C(17)	1.444(11)	C(26)–C(27)	1.486(11)
C(17)–O(15)	1.198(11)	C(27)–O(25)	1.190(11)
C(17)–O(16)	1.341(9)	C(27)–O(26)	1.315(11)
C(18)–O(16)	1.460(12)	C(28)–O(26)	1.440(11)
C(19)–C(110)	1.474(14)	C(29)–C(210)	1.548(13)
C(19)–C(111)	1.523(15)	C(29)–C(211)	1.533(13)
C(19)–N(11)	1.497(12)	C(29)–N(21)	1.485(11)
C(112)–C(113)	1.347(12)	C(212)–C(213)	1.372(12)
C(112)–N(11)	1.385(11)	C(212)–N(21)	1.376(11)
C(113)–N(12)	1.393(10)	C(213)–N(22)	1.408(10)
C(114)–C(115)	1.507(14)	C(214)–C(215)	1.506(14)
C(114)–C(116)	1.500(12)	C(214)–C(216)	1.505(12)
C(114)–N(12)	1.516(11)	C(214)–N(22)	1.512(11)

^ae.s.d.s given in parentheses.

to a Ru–Ru distance of 2.936(1) Å in the corresponding Ru complex) or by a weaker coordination of the alkyne in the Fe complex.

The Fe atoms and the atoms of the coordinated alkyne are almost coplanar (r.m.s. deviation: 0.04 Å). To our knowledge, the only other example of a complex with a methyl propynoate molecule in a bridging position along an Fe–Fe bond is Fe₂Mn(CO)₆(η⁵-C₅H₅)(μ₂-HC≡CC(O)OMe) [24]. In this trinuclear complex, however, the former alkyne fragment is not only μ₂-bridging between the two Fe atoms, but is also η²-coordinated to the Mn center. Therefore, comparison of the C=C bond length of 1.362(4) Å in this latter complex with this bond in the present dinuclear Fe and Ru complexes is not appropriate.

It is worth noting that in the Fe complex only one of the two possible regioisomers with respect to the coordination of the alkyne is observed, namely the complex with the unsubstituted alkyne C(15) atom bonded to the Fe(11) center, to which both N atoms of the DAB ligand are σ-coordinated. The reason for this regioselectivity is not clear. It seems plausible to assume that Fe(11), to which two hard σ-N donor atoms are bonded, is more electron rich than Fe(12). Accordingly, one would expect the substituted alkyne C atom, which is more electrophilic due to the inductive electron withdrawing effect of the methoxycarbonyl group, to be bonded to Fe(11). The fact that this is not observed, may be rationalized by assuming that the isolated isomer is a kinetic rather than a thermodynamic product. A second explanation may be that in the alkyne the mesomeric electron withdrawing effect of the sub-

TABLE 3. Bond Angles (°) of the Non-hydrogen Atoms of 3a^a

Fe(12)–Fe(11)–C(11)	133.5(4)	Fe(11)–Fe(12)–N(11)	46.7(2)
Fe(12)–Fe(11)–C(12)	136.1(4)	Fe(11)–Fe(12)–N(12)	46.9(3)
Fe(12)–Fe(11)–C(15)	72.4(4)	Fe(22)–Fe(21)–C(21)	136.0(3)
Fe(12)–Fe(11)–N(11)	51.3(3)	Fe(22)–Fe(21)–C(22)	133.6(3)
Fe(12)–Fe(11)–N(12)	51.0(3)	Fe(22)–Fe(21)–C(25)	71.5(3)
C(11)–Fe(11)–C(12)	85.9(6)	Fe(22)–Fe(21)–N(21)	51.2(2)
C(11)–Fe(11)–C(15)	89.7(6)	Fe(22)–Fe(21)–N(22)	50.9(2)
C(11)–Fe(11)–N(11)	96.7(5)	C(21)–Fe(21)–C(22)	85.0(6)
C(11)–Fe(11)–N(12)	168.4(5)	C(21)–Fe(21)–C(25)	91.9(5)
C(12)–Fe(11)–C(15)	92.9(6)	C(21)–Fe(21)–N(21)	163.6(4)
C(12)–Fe(11)–N(11)	161.0(4)	C(21)–Fe(21)–N(22)	96.5(5)
C(12)–Fe(11)–N(12)	94.9(5)	C(22)–Fe(21)–C(25)	90.2(5)
C(15)–Fe(11)–N(11)	105.9(5)	C(22)–Fe(21)–N(21)	96.4(5)
C(15)–Fe(11)–N(12)	101.8(4)	C(22)–Fe(21)–N(22)	167.6(4)
N(11)–Fe(11)–N(12)	79.0(4)	C(25)–Fe(21)–N(21)	104.4(4)
Fe(11)–Fe(12)–C(13)	134.1(3)	C(25)–Fe(21)–N(22)	102.1(4)
Fe(11)–Fe(12)–C(14)	133.4(4)	N(21)–Fe(21)–N(22)	78.7(4)
Fe(11)–Fe(12)–C(16)	67.0(3)	Fe(21)–Fe(22)–C(23)	135.6(3)
Fe(11)–Fe(12)–C(112)	72.8(4)	Fe(21)–Fe(22)–C(24)	132.4(3)
Fe(11)–Fe(12)–C(113)	73.0(4)	Fe(21)–Fe(22)–C(26)	68.0(3)

(continued)

TABLE 3. (continued)

Fe(21)–Fe(22)–C(212)	72.4(3)	C(113)–N(12)–C(114)	114.4(8)
Fe(21)–Fe(22)–C(213)	73.3(3)	C(17)–O(16)–C(18)	118.2(8)
Fe(21)–Fe(22)–N(21)	46.1(2)	C(23)–Fe(22)–C(24)	87.8(6)
Fe(21)–Fe(22)–N(22)	46.6(2)	C(23)–Fe(22)–C(26)	96.5(6)
C(13)–Fe(12)–C(14)	88.1(6)	C(23)–Fe(22)–C(212)	97.6(6)
C(13)–Fe(12)–C(16)	94.6(5)	C(23)–Fe(22)–C(213)	125.3(5)
C(13)–Fe(12)–C(112)	127.6(5)	C(23)–Fe(22)–N(21)	99.6(5)
C(13)–Fe(12)–C(113)	98.8(6)	C(23)–Fe(22)–N(22)	164.4(4)
C(13)–Fe(12)–N(11)	165.8(4)	C(24)–Fe(22)–C(26)	93.2(6)
C(13)–Fe(12)–N(12)	98.4(5)	C(24)–Fe(22)–C(212)	129.5(5)
C(14)–Fe(12)–C(16)	95.8(5)	C(24)–Fe(22)–C(213)	99.0(5)
C(14)–Fe(12)–C(112)	98.4(6)	C(24)–Fe(22)–N(21)	166.4(4)
C(14)–Fe(12)–C(113)	127.3(5)	C(24)–Fe(22)–N(22)	97.8(5)
C(14)–Fe(12)–N(11)	97.9(5)	C(26)–Fe(22)–C(212)	135.4(4)
C(14)–Fe(12)–N(12)	165.8(5)	C(26)–Fe(22)–C(213)	136.7(4)
C(16)–Fe(12)–C(112)	135.6(4)	C(26)–Fe(22)–N(21)	97.3(4)
C(16)–Fe(12)–C(113)	134.9(4)	C(26)–Fe(22)–N(22)	97.7(5)
C(16)–Fe(12)–N(11)	97.5(4)	C(212)–Fe(22)–C(213)	39.1(4)
C(16)–Fe(12)–N(12)	96.2(4)	C(212)–Fe(22)–N(21)	38.6(3)
C(112)–Fe(12)–C(113)	38.5(4)	C(212)–Fe(22)–N(22)	67.7(4)
C(112)–Fe(12)–N(11)	38.9(3)	C(213)–Fe(22)–N(21)	67.4(4)
C(112)–Fe(12)–N(12)	67.6(4)	C(213)–Fe(22)–N(22)	39.6(3)
C(113)–Fe(12)–N(11)	67.4(4)	N(21)–Fe(22)–N(22)	72.3(4)
C(113)–Fe(12)–N(12)	39.4(4)	Fe(21)–C(21)–O(21)	176.1(6)
N(11)–Fe(12)–N(12)	73.0(4)	Fe(21)–C(22)–O(22)	175.6(7)
Fe(11)–C(11)–O(11)	175.8(7)	Fe(22)–C(23)–O(23)	177.8(6)
Fe(11)–C(12)–O(12)	175.6(7)	Fe(22)–C(24)–O(24)	178.1(7)
Fe(12)–C(13)–O(13)	178.7(7)	Fe(21)–C(25)–C(26)	107.9(7)
Fe(12)–C(14)–O(14)	179.2(7)	Fe(22)–C(26)–C(25)	112.5(7)
Fe(11)–C(15)–C(16)	108.0(7)	Fe(22)–C(26)–C(27)	126.1(6)
Fe(12)–C(16)–C(15)	112.4(7)	C(25)–C(26)–C(27)	121.4(9)
Fe(12)–C(16)–C(17)	122.3(6)	C(26)–C(27)–O(25)	123.3(9)
C(15)–C(16)–C(17)	125.0(9)	C(26)–C(27)–O(26)	114.4(9)
C(16)–C(17)–O(15)	127.6(9)	O(25)–C(27)–O(26)	122.3(10)
C(16)–C(17)–O(16)	114.7(8)	C(210)–C(29)–C(211)	110.1(10)
O(15)–C(17)–O(16)	117.6(9)	C(210)–C(29)–N(21)	112.7(9)
C(110)–C(19)–C(111)	113.9(11)	C(211)–C(29)–N(21)	109.8(9)
C(110)–C(19)–N(11)	113.7(10)	Fe(22)–C(212)–C(213)	70.2(7)
C(111)–C(19)–N(11)	108.6(11)	Fe(22)–C(212)–N(21)	73.0(7)
Fe(12)–C(112)–C(113)	70.5(7)	C(213)–C(212)–N(21)	114.4(10)
Fe(12)–C(112)–N(11)	72.9(7)	Fe(22)–C(213)–C(212)	70.7(7)
C(113)–C(112)–N(11)	114.6(10)	Fe(22)–C(213)–N(22)	72.3(6)
Fe(12)–C(113)–C(112)	71.0(8)	C(212)–C(213)–N(22)	112.8(9)
Fe(12)–C(113)–N(12)	72.5(7)	C(215)–C(214)–C(216)	111.4(10)
C(112)–C(113)–N(12)	114.4(9)	C(215)–C(214)–N(22)	113.1(9)
C(115)–C(114)–C(116)	113.9(10)	C(216)–C(214)–N(22)	109.3(9)
C(115)–C(114)–N(12)	109.8(10)	Fe(21)–N(21)–Fe(22)	82.6(4)
C(116)–C(114)–N(12)	112.2(9)	Fe(21)–N(21)–C(29)	131.8(6)
Fe(11)–N(11)–Fe(12)	81.9(4)	Fe(21)–N(21)–C(212)	116.5(6)
Fe(11)–N(11)–C(19)	129.6(6)	Fe(22)–N(21)–C(29)	122.2(6)
Fe(11)–N(11)–C(112)	115.0(6)	Fe(22)–N(21)–C(212)	68.5(6)
Fe(12)–N(11)–C(19)	124.7(6)	C(29)–N(21)–C(212)	111.2(9)
Fe(12)–N(11)–C(112)	68.2(7)	Fe(21)–N(22)–Fe(22)	82.4(4)
C(19)–N(11)–C(112)	114.6(9)	Fe(21)–N(22)–C(213)	115.5(6)
Fe(11)–N(12)–Fe(12)	82.1(4)	Fe(21)–N(22)–C(214)	131.8(5)
Fe(11)–N(12)–C(113)	114.7(6)	Fe(22)–N(22)–C(213)	68.1(6)
Fe(11)–N(12)–C(114)	130.1(6)	Fe(22)–N(22)–C(214)	122.2(5)
Fe(12)–N(12)–C(113)	68.2(7)	C(213)–N(22)–C(214)	112.3(9)
Fe(12)–N(12)–C(114)	124.8(6)	C(27)–O(26)–C(28)	117.0(9)

^ae.s.d.s given in parentheses.

TABLE 4. ^1H NMR Data of $\text{M}_2(\text{CO})_4(\text{i-Pr-DAB})(\mu_2\text{-R}'\text{C}\equiv\text{CR}'')$ [3a: M = Fe, R' = H, R'' = C(O)OMe; 3b: M = Ru, R' = R'' = H; 3c: M = Ru, R' = Ph, R'' = H; 3d: M = Ru, R' = H, R'' = Ph]^a

	Me(i-Pr)	CH(i-Pr)	N=CH	Alkyne R'	Alkyne R''
3a	0.93 (d, $J = 6$ Hz) 1.34 (d, $J = 6$ Hz)	2.54 (sept, $J = 6$ Hz)	6.06(s)	9.37(s)	3.89(s) (R'' = C(O)OMe)
3b ^b	0.63 (d, $J = 6$ Hz) 1.19 (d, $J = 6$ Hz)	2.23 (sept, $J = 6$ Hz)	6.16(s)	8.22(s)	7.50(s)
3c	0.90 (d, $J = 6$ Hz) 1.37 (d, $J = 6$ Hz)	2.40 (sept, $J = 6$ Hz)	6.27(s)	7.40(m) (R' = Ph)	7.64(s)
3d	1.00 (d, $J = 6$ Hz) 1.40 (d, $J = 6$ Hz)	2.40 (sept, $J = 6$ Hz)	6.27(s)	8.22(s)	7.40(m) (R'' = Ph)

^aValues in ppm, relative to Me_4Si , measured in CDCl_3 at 20 °C, spectrometer frequency 100 MHz. ^bReported previously [8].

TABLE 5. ^{13}C NMR Data of $\text{M}_2(\text{CO})_4(\text{i-Pr-DAB})(\mu_2\text{-R}'\text{C}\equiv\text{CR}'')$ [3a: M = Fe, R' = H, R'' = C(O)OMe; 3b: M = Ru, R' = R'' = H; 3c: M = Ru, R' = Ph, R'' = H; 3d: M = Ru, R' = H, R'' = Ph]^a

	Me(i-Pr)	CH(i-Pr)	N=CH	Alkyne C	R', R''	COs
3a ^{b, c}	24.6 27.4	62.4	100.9	127.7 (CR'') 145.5 (CH)	52.3 (OMe) 161.8 (C(O)O)	213.4 220.2
3b ^c	26.2 28.6	61.9	100.3	102.4 111.8		205.1 210.9
3c ^d	28.9 26.6	62.2	101.2	100.2 (CH) 135.5 (CR')	125–132 (Ph)	201.9 204.5
3d ^d	28.9 26.4	62.3	101.1	107.4 (CH) 121.4 (CR'')	125–132 (Ph)	201.9 206.0

^aValues in ppm, relative to Me_4Si , measured in CD_2Cl_2 at 20 °C. ^bMeasured in CDCl_3 at –20 °C. ^cSpectrometer frequency 63 MHz. ^dSpectrometer frequency 25 MHz.

stituent is more important than the inductive effect and causes the unsubstituted C atom to be the most electrophilic center.

NMR Spectroscopy

The ^1H and ^{13}C NMR data of 3a–d are listed in Tables 4 and 5, respectively. The ^1H NMR data of 3a in solution are consistent with the molecular structure in the solid state. The symmetry plane in the complex causes both halves of the i-Pr-DAB ligand to be equivalent. This also applies for 3b–d. Consequently, in all complexes both imine protons appear as one singlet between 6.0 and 6.3 ppm, which is as expected for 8e bonded R-DAB ligands [7]. The resonances of the diastereotopic i-Pr methyl groups appear as two doublets in the expected region around 1 ppm, whereas the corresponding methine protons are found as a septet at about 2.4 ppm.

In the following discussion, the metal centers σ -bonded to the DAB N atoms will be referred to as Fe or Ru, the centers to which the C=N bonds are π -bonded as Fe' or Ru'. The alkyne moieties bonded to the metal centers are referred to as CR' and CR'', respectively (see Fig. 3). In 3a, the

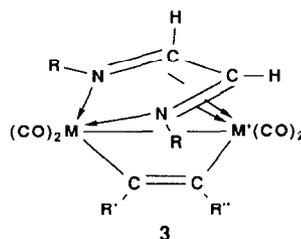


Fig. 3. The positions of M, M', CR' and CR'' in 3.

proton on C(15) resonates at 9.37 ppm, while in 3b the acetylene protons appear at 7.50 and 8.22 ppm. The signal at 8.22 ppm is assigned to the proton on the C atom bonded to Ru. As this Ru center will possess a higher electron density than Ru', it will cause a more pronounced paramagnetic deshielding, and thus a downfield shift, of the alkyne CR' moiety bonded to Ru, when compared to the CR'' fragment bonded to Ru'. This conclusion is in agreement with the fact that in the ^{13}C NMR of the Fe analogue 3a, the unsubstituted alkyne C atom resonates about 18 ppm downfield with respect to the substituted one. This downfield shift is not caused by the metho-

xy carbonyl substituent on the alkyne, as it is known that substitution of one of the protons in ethene by an alkoxy carbonyl group (we can regard the coordinated alkyne $\text{RC}\equiv\text{CH}$ as a trisubstituted ethene fragment) causes an approximately equal downfield shift of both C atoms [25]. In the ^1H NMR of the mixture of **3c** and **3d**, two alkyne H signals are observed at 7.64 and 8.22 ppm (integral ratio 2:1). In view of the above mentioned arguments, the signal at 8.22 ppm is due to the alkyne proton in the proximity of Ru and hence belongs to **3d**. The signal at 7.64 ppm is thus assigned to the alkyne proton in **3c**, in which the alkyne CH moiety is bonded to Ru'. The protons of the alkyne substituents in **3a–d** are found in the expected ranges.

In the ^{13}C NMR of **3a–d** the two isopropyl-methyl signals, due to two pairs of diastereotopic methyl groups, appear in the expected region (20–30 ppm), while the methine C atoms resonate at about 62 ppm. The imine C atoms are found at about 100 ppm, which is normal for imine C atoms of an 8e donating R-DAB ligand [9]. The CO ligands appear in the ^{13}C spectra as two signals, each caused by two equivalent CO groups.

The alkyne C atoms resonate in the range of 100–150 ppm. As mentioned above, the C atoms bonded to the metal center that is σ -bonded to both R-DAB nitrogen atoms appear downfield with respect to the other alkyne C atom. Only in the ^{13}C spectrum of **3c**, the alkyne C atom bonded to the Ru center appears at the higher field. This is due to the large substituent effect of a phenyl group attached to an ethene fragment (+12.5 ppm for C_α and –11 ppm for C_β) [25]. The chemical shifts of the C atoms of the methoxycarbonyl and phenyl groups are as expected.

Discussion

In a previous paper [12] it was proposed that the formation of $\text{Ru}_2(\text{CO})_4(\text{i-Pr-DAB})(\mu_2\text{-HC}\equiv\text{CH})$ (**3b**) in the reaction of $\text{Ru}_2(\text{CO})_6(\text{i-Pr-DAB})$ (**1b**) with acetylene proceeded via an unstable intermediate $\text{Ru}_2(\text{CO})_5[\text{AIB}(\text{i-Pr},\text{H},\text{H})]$ (**6**)*. This intermediate molecule would then form **3b** with the 8e donating DAB ligand and the μ_2 -bridging acetylene, after C–C bond cleavage and elimination of a CO molecule. This proposal, which we now regard as incorrect, was based on the facts that small amounts of benzene were formed in the reaction and that the above mentioned AIB complexes were supposed to be intermediates in the cyclotrimerization

*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 $\text{R}'\text{C}\equiv\text{CR}''$. The backbone of the ligand is $\text{RN}=\text{C}(\text{H})\text{C}(\text{H})(\text{NR})\text{C}(\text{R}')=\text{CR}''$, which is 3-Amino-4-Imino-1-Butene.

of alkynes catalyzed by $\text{Ru}_2(\text{CO})_6(\text{R-DAB})$. Later, however, it was found that $\text{Ru}_2(\text{CO})_6(\text{i-Pr-DAB})$ readily loses a CO upon either heating of these complexes or treatment with Me_3NO , yielding $\text{Ru}_2(\text{CO})_5(\text{i-Pr-DAB})$ (**2b**) [5]. In **2b** the DAB ligand is coordinated as an 8e donor and one of the COs is in an asymmetrically bridging position. $\text{Ru}_2(\text{CO})_5(\text{i-Pr-DAB})$ could be isolated and upon further reaction with acetylene **3b** was formed and not a complex of type **6** (see Scheme 1).

The substitution of a bridging CO by an alkyne in $\text{M}_2(\text{CO})_5(\text{i-Pr-DAB})$ [M = Fe, Ru] (see Scheme 1) is not surprising, knowing the reactivity of **2b** [5]. The reactions with an alkyne may be regarded as being analogous to the reaction of $\text{Ru}_2(\text{CO})_5(\text{R-DAB})$ with $\text{Ru}_3(\text{CO})_{12}$, where the bridging CO is substituted by a $\text{Ru}(\text{CO})_4$ unit, yielding $\text{Ru}_3(\text{CO})_8(\text{R-DAB})$ [5]. This analogy can be understood regarding the similarity in shape and symmetry of the frontier orbitals of a $\text{Ru}(\text{CO})_4$ unit and an alkyne, when regarded as a diradical donating 2 electrons to the $\text{Ru}_2(\text{CO})_4(\text{R-DAB})$ unit [21, 26].

We have now shown that $\text{Ru}_2(\text{CO})_6(\text{i-Pr-DAB})$ reacts with phenylacetylene in heptane at 90 °C to give the complexes $\text{Ru}_2(\text{CO})_4(\text{i-Pr-DAB})(\mu_2\text{-PhC}\equiv\text{CH})$ (**3c, d**). Formation of the complex $\text{Ru}_2(\text{CO})_5[\text{AIB}(\text{i-Pr},\text{Ph},\text{H})]$ (**6**) is not observed. This latter complex would be structurally analogous to $\text{Ru}_2(\text{CO})_5[\text{AIB}(\text{t-Bu},\text{Ph},\text{H})]$, which is formed when $\text{Ru}_2(\text{CO})_6(\text{t-Bu-DAB})$ is reacted with phenylacetylene at 90 °C, and of which the crystal structure has been published [12]. In this latter reaction no $\text{Ru}_2(\text{CO})_4(\text{t-Bu-DAB})(\mu_2\text{-PhC}\equiv\text{CH})$ is formed. The reason for this different chemical behaviour of the i-Pr and t-Bu analogues is that $\text{Ru}_2(\text{CO})_5(\text{i-Pr-DAB})$ is readily formed when $\text{Ru}_2(\text{CO})_6(\text{i-Pr-DAB})$ is heated, whereas $\text{Ru}_2(\text{CO})_5(\text{t-Bu-DAB})$ is not accessible thermally, causing $\text{Ru}_2(\text{CO})_6(\text{t-Bu-DAB})$ to react directly with phenylacetylene to give the AIB complex **6**. These observations, combined with the fact that heating of $\text{Ru}_2(\text{CO})_5[\text{AIB}(\text{i-Pr},\text{C}(\text{O})\text{OMe},\text{C}(\text{O})\text{OMe})]$ does not lead to the formation of $\text{Ru}_2(\text{CO})_4(\text{i-Pr-DAB})(\mu_2\text{-MeOC}(\text{O})\text{C}\equiv\text{CC}(\text{O})\text{OMe})$, show that the complexes with a μ_2 -bridging alkyne and an 8e donating DAB ligand are formed via $\text{Ru}_2(\text{CO})_5(\text{i-Pr-DAB})$ (**2b**) rather than via a $\text{Ru}_2(\text{CO})_5[\text{AIB}]$ complex (**6**). These latter complexes are formed via $\text{Ru}_2(\text{CO})_6[\text{AIB}(\text{R},\text{R}',\text{R}'')]$ (**5**) which is formed through the insertion of the alkyne in the metal–metal bond of $\text{Ru}_2(\text{CO})_6(\text{R-DAB})$ or via a direct attack of the alkyne on the coordinated imine C atom and the Ru carbonyl core in **1b**. This subject will be discussed in a forthcoming paper [22]. The above mentioned reactions are shown in Scheme 1.

$\text{Fe}_2(\text{CO})_5(\text{i-Pr-DAB})$ (**2a**) has until now never been isolated, nor proven to be an intermediate in reactions of $\text{Fe}_2(\text{CO})_6(\text{i-Pr-DAB})$. Nevertheless, the analogy between the reactions of the Fe and Ru

complexes presented here strongly suggests that such a highly reactive complex is indeed the intermediate in the formation of **3a**. This is further supported by the fact that the formation of **3a** is only observed when nitrogen is passed through the solution, because it is only under these circumstances that the equilibrium between $\text{Fe}_2(\text{CO})_6(\text{i-Pr-DAB})$ and $\text{Fe}_2(\text{CO})_5(\text{i-Pr-DAB})$ is shifted to the side of the latter compound by the continuous removal of the formed CO from the solution.

In the reactions of polynuclear transition metal carbonyls with alkynes trinuclear complexes with an alkyne bridging two metals along the metal–metal axis are quite commonly observed [24, 27–32]. These complexes are regarded as possible intermediates in oligomerization reactions of alkynes catalyzed by transition metal clusters [30]. However, not so many examples of dinuclear complexes containing an alkyne coordinated in this mode are known. A reason for this relative scarcity may be the lack of additional stabilization in dinuclear complexes, that is possible in trinuclear complexes, where the resulting olefinic bond can be further η^2 -coordinated to the third metal atom. However, the stability of the present dinuclear complexes $\text{M}_2(\text{CO})_4(\text{i-Pr-DAB})(\mu_2\text{-R}'\text{C}\equiv\text{CH})$ may result from the presence of the bridging i-Pr-DAB ligand. This can be rationalized by assuming a mutual stabilizing effect of the δe bonded i-Pr-DAB ligand and the alkyne, which results from the combination of the hard alkyne donor ligand and the good π -accepting properties of the DAB ligand. This causes a reduction of the reactivity of the coordinated alkyne as well as a strong coordination of the DAB ligand to the dinuclear metal unit, through which open coordination sites are less likely produced. This view is supported by the results of a theoretical study on the electronic structure of and bonding within $\text{Ru}_2(\text{CO})_4(\text{Me-DAB})(\mu_2\text{-HC}\equiv\text{CH})$ [33]. An important conclusion from this study is that the bonding scheme of this latter molecule is dominated by the absence of a direct metal–metal interaction and by strong back-bonding interactions from the Ru atoms to the DAB and alkyne ligands. As a secondary effect, the steric bulk of the coordinated R-DAB may well prevent other reactants approaching the bridging alkyne.

Conclusions

We have shown that, provided the correct kinetic path is chosen, the formation of Fe complexes with a $\sigma, \sigma\text{-N, N}', \eta^2, \eta^2\text{-C=N, C=N}'$ coordinated R-DAB ligand is possible. This is not surprising, in view of the many known examples of Ru and Os complexes with an δe donating R-DAB ligand as well as of the isoelectronic dinuclear ferracyclopentadienyl complexes [19]. Thus, examples of complexes con-

taining an δe donating R-DAB ligand are now known for all members of the iron triad (Fe, Ru, Os). It is now also clear that the complexes $\text{M}_2(\text{CO})_4(\text{i-Pr-DAB})(\mu_2\text{-R}'\text{C}\equiv\text{CH})$ (**3**) [$\text{M} = \text{Fe}$, $\text{R}' = \text{C}(\text{O})\text{OMe}$; $\text{M} = \text{Ru}$, $\text{R}' = \text{H}$, Ph] are most likely formed via $\text{M}_2(\text{CO})_5(\text{i-Pr-DAB})$ (**2**), rather than via $\text{M}_2(\text{CO})_5\text{-[AIB(i-Pr, R', H)]}$ (**6**). This conclusion points in the case of Fe to the existence of $\text{Fe}_2(\text{CO})_5(\text{i-Pr-DAB})$ as an important intermediate, which is isostructural to $\text{Ru}_2(\text{CO})_5(\text{i-Pr-DAB})$. The latter complex has recently been shown to be a key intermediate in the $\text{Ru}_3(\text{CO})_{12}/\text{R-DAB}$ reaction sequences [5]. Likewise, $\text{Fe}_2(\text{CO})_5(\text{R-DAB})$ may also be an intermediate in other reactions of $\text{Fe}_2(\text{CO})_6(\text{R-DAB})$.

Supplementary Material

A table of the anisotropic thermal parameters of the non-H atoms, a table of the calculated fractional coordinates and isotropic thermal parameters of the H atoms and a listing of structure factor amplitudes (10 pages) can be ordered from the authors.

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