Inorganica Chimica Acta, 149 (1988) 193–208

Synthesis of Heterodinuclear FeRu(CO)$_6$(R-DAB(6e))(R-DAB = RN=C(H)C(H)=NR) Part XV. Comparison of the Reactivities of Heterodinuclear FeRu(CO)$_6$(R-DAB(6e)) and Homodinuclear Analogues M$_2$(CO)$_6$(R-DAB(6e)) (M = Fe, Ru). Single-crystal X-ray Structures of FeRu(CO)$_6$(i-Pr-DAB(6e)) and FeRu(CO)$_5$(i-Pr-DAB(4e))(C$_3$H$_4$)*

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(Received January 12, 1988)

Abstract

The reactions of Fe(CO)$_3$(R-DAB; R^1, H(4e)) (**1a**: R = i-Pr, R^1 = H; **1b**: R = t-Bu, R^1 = H; **1c**: R = c-Hex, R^1 = H; **1e**: R = *p*-Tol, R^1 = H; **1f**: R = i-Pr, R^1 = Me) with Ru$_3$(CO)$_{12}$ and of Ru(CO)$_3$(R-DAB; R^1, H(4e)) (**2a**: R = i-Pr, R^1 = H; **2d**: R = CH(i-Pr)$_2$, R^1 = H) with Fe$_2$(CO)$_9$ in refluxing heptane both afforded FeRu(CO)$_6$(R-DAB; R^1, H(6e)) (**3**) in yields between 50 and 65%.

The coordination mode of the ligand has been studied by a single crystal X-ray structure determination of FeRu(CO)$_6$(i-Pr-DAB(6e)) (**3a**). Crystals of **3a** are monoclinic, space group $P2_1/a$, with four molecules in a unit cell of dimensions: $a = 22.436(3)$, $b = 8.136(3)$, $c = 10.266(1)$ Å and $\beta = 99.57(1)°$. The structure was refined to $R = 0.049$ and $R_w = 0.052$ using 3045 reflections above the $2.5\sigma(I)$ level. The molecule contains an Fe–Ru bond of 2.6602(9) Å, three terminally bonded carbonyls to Fe, three terminally bonded carbonyls to Ru and a bridging 6e donating i-Pr-DAB ligand. The i-Pr-DAB ligand is coordinated to Ru via N(1) and N(2) occupying an apical and equatorial site respectively (Ru–N(1) = 2.138(4) and Ru–N(2) = 2.102(3) Å). The C(2)=N(2) moiety of the ligand is η^2-coordinated to Fe with C(2) in an apical and N(2) in an equatorial site (Fe–C(2) = 2.070(5) and Fe–N(2) = 1.942(3) Å).

The ^{1}H and ^{13}C NMR data indicate that in all FeRu(CO)$_6$(R-DAB(6e)) complexes (**3a** to **3f**) exclusively η^2-C=N coordination to the Fe atom and not to the Ru atom is present irrespective of whether **3** was prepared by reaction of Fe(CO)$_3$(R-DAB(4e)) (**1**) with Ru$_3$(CO)$_{12}$ or by reaction of Ru(CO)$_3$(R-DAB(4e)) (**2**) with Fe$_2$(CO)$_9$. In the case of FeRu(CO)$_6$(i-Pr-DAB; Me, H(6e)) (**3f**) the NMR data show that only the complex with the C(Me)=N moiety of the ligand σ-N coordinated to the Ru atom and the C(H)=N moiety η^2-coordinated to the Fe atom was formed. Variable temperature NMR experiments up to 140 °C showed that the α-diimine ligand in **3a** is stereochemically rigid bonded.

FeRu(CO)$_6$(R-DAB(6e)) (**3a** and **3e**) reacted with allene to give FeRu(CO)$_5$(R-DAB(4e))(C$_3$H$_4$) (**4a** and **4e**). A single crystal X-ray structure determination of FeRu(CO)$_5$(i-Pr-DAB(4e))(C$_3$H$_4$) (**4a**) was performed. Crystals of **4a** are triclinic, space group $P\bar{1}$, with two molecules in a unit cell of dimensions: $a = 9.7882(7)$, $b = 12.2609(9)$, $c = 8.3343(7)$ Å, $\alpha = 99.77(1)°$, $\beta = 91.47(1)°$ and $\gamma = 86.00(1)°$. The structure was refined to $R = 0.028$ and $R_w = 0.043$ using 4598 reflections above the $2\sigma(I)$ level. The molecule contains an Fe–Ru bond of 2.7405(7) Å and three terminally bonded carbonyls to iron. Two carbonyls are terminally bonded to the Ru atom together with a chelating 4e donating i-Pr-DAB ligand [Ru–N = 2.110(1) (mean)]. The allene ligand is coordinated in an η^3-allylic fashion to the Fe atom while the central carbon of the allene moiety is σ-bonded to the Ru atom (Fe–C(14) = 2.166(3), Fe–C(15) = 1.970(2), Fe–C(16) = 2.127(3) and Ru–C(15) = 2.075(2) Å). The ^{1}H and ^{13}C NMR data show that in solution the coordination modes of the R-DAB and the allene ligands are the same as in the solid state.

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*1,4-Disubstituted-1,4-diaza-1,3-butadienes, R–N=C(R^1)–C(R^2)=N–R, are abbreviated as R-DAB{R^1, R^2}. When R^1 = R^2 = H the abbreviation R-DAB can be used. The number of electrons donated by the R-DAB ligand to the complex is indicated between brackets, *i.e.* R-DAB(4e) stands for σ,σ-N,N′ chelating 4e coordinated; R-DAB(6e) stands for σ-N,μ_2-N′,η^2-C=N′ bridging 6e coordinated; R-DAB(8e) stands for σ,σ-N,N′-η^2,η^2-C=N, C′=N′ bridging 8e coordinated. For earlier parts see ref. 6a.

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0020-1693/88/$3.50

Thermolysis reactions of **3a** with R-DAB or carbodiimides gave decomposition and did not afford C(imine)–C(reactant) coupling products. Thermolysis reactions of **3a** with $M_3(CO)_{12}$ (M = Ru, Os) and Me_3NO gave decomposition. When the reaction of **3a** with Me_3NO was performed in the presence of dimethylacetylenedicarboxylate (DMADC) the known complex $FeRu(CO)_4$(i-Pr-DAB(8e))-(DMADC) (**5a**) was formed in low yield. In **5a** the R-DAB ligand is in the 8e coordination mode with both the imine bonds η^2-coordinated to iron. The acetylene ligand is coordinated in a bridging fashion, parallel with the Fe–Ru bond.

Introduction

There is a long standing interest in the preparation and study of mixed metal clusters [1, 2]. Firstly, the presence of different metal atoms may allow the study of the influence of each metal on a number of chosen reactions. Secondly, (novel) reactions may be found which require the presence of two or more different metals in one complex. A specific example is the water–gas shift reaction catalysed by $H_2FeRu_3(CO)_{12}$ in basic and acidic environments for which the presence of both iron and ruthenium in the complex is essential [3].

In the course of our investigations into the structure–reactivity relationships of metal carbonyl α-diimine complexes it was found that the type of reactivity depended not only on the type of ligand, but also on the metal atom [4a–c]. It appeared therefore to us of great interest to study the effect of two different metal atoms on the reactivity of polynuclear metal carbonyl R-DAB complexes. This type of study, however, was hindered up to now by the absence of easily available suitable heteronuclear R-DAB complexes.

In the past we reported the synthesis of heterodinuclear $FeRu(CO)_6$(R-DAB(6e)) (**3**), which appeared to be isostructural with the previously synthesized homodinuclear $M_2(CO)_6$(R-DAB(6e)) (M = Fe, Ru and Os) compounds, which contain a 6e donor R-DAB ligand coordinated to the $M_2(CO)_6$ unit having a metal–metal bond, see Fig. 1 [5a–d]. These $M_2(CO)_6$(R-DAB(6e)) compounds show a rich and varied chemistry, but unfortunately $FeRu(CO)_6$-(R-DAB(6e)) (**3**) could not be prepared in sufficient yields to allow detailed chemical studies. Moreover, the question to which of the two metals the η^2-C=N bonding occurred could not be answered which made interpretation of the observed reactivity impossible.

In this paper we report a high yield synthesis of **3** and the results of the single crystal X-ray structure determination of $FeRu(CO)_6$(i-Pr-DAB(6e)) (**3a**), from which the precise mode of bonding of R-DAB to an $FeRu(CO)_6$ unit could be derived. This gave us the opportunity to carry out reactivity studies of **3** with a number of substrates which we present in this and forthcoming publications [6b, 7].

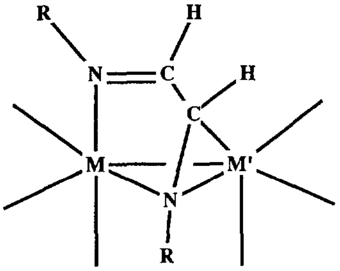

Fig. 1. Schematic structures of $MM'(CO)_6$(R-DAB(6e)) (M = M' = Fe, Ru, Os; M = Ru, M' = Fe).

Experimental

Materials and Apparatus

NMR spectra were obtained on a Bruker AC100, AC200 and WM250 spectrometer. IR spectra were recorded with a Perkin-Elmer 283 spectrometer; FT-IR spectra were obtained on a Nicolet 7199B FT-IR interferometer (liquid nitrogen cooled Hg, Cd, Te detector). Field desorption (FD) mass spectra were obtained with a Varian MAT 711 double focussing mass spectrometer with a combined EI/FD/FI ion source and coupled to a spectrosystem MAT 100 data acquisition unit [8]. Elemental analyses were carried out by the section Elemental Analyses of the Institute of Applied Chemistry, TNO, Zeist. The Netherlands. All preparations were carried out in an atmosphere of purified nitrogen, using carefully dried solvents. Silicagel (60 Mesh) for column chromatography was activated before use. $Ru_3(CO)_{12}$ and $Os_3CO)_{12}$ were purchased from Strem Chemicals and used without further purification. The R-DAB{R^1, H} ligands (**a**: R = i-Pr, R^1 = H; **b**: R = t-Bu, R^1 = H; c: R = c-Hex, R^1 = H; **d**: R = CH(i-Pr)$_2$, R^1 = H; **e**: R = *p*-Tol, R^1 = H; f: R = i-Pr, R^1 = Me) were prepared by the condensation reaction of glyoxal with the appropriate amine [9a, b]. $Fe(CO)_3$(R-DAB; R^1, H(4e)) (**1**) and $Ru(CO)_3$R-DAB; R^1, H(4e)) (**2**) were prepared according to literature methods [10a, b].

*Synthesis of $FeRu(CO)_6$(R-DAB; R^1, H(6e)) (**3a** to **3f**; **a**: R = i-Pr, R^1 = H; **b**: R = t-Bu, R^1 = H; **c**: R = c-Hex, R^1 = H; **d**: R = CH(i-Pr)$_2$, R^1 = H; **e**: R = p-Tol, R^1 = H; **f**: R = i-Pr, R^1 = Me)*

Compounds **3a** to **3f** could be synthesized by basically the same procedure, *i.e.* by reaction of $Fe(CO)_3$(R-DAB; R^1, H(4e)) (**1a**, **1b**, **1c**, **1e** and **1f**) with $Ru_3(CO)_{12}$ or reaction of $Ru(CO)_3$(R-DAB; R^1, H(4e)) (**2a** and **2d**) with $Fe_2(CO)_9$.

FeRu(CO)$_6$(R-DAB(6e)) (3a, 3b, 3c, 3e and 3f) by reaction of Ru$_3$(CO)$_{12}$ with Fe(CO)$_3$(R-DAB; R^1, H(4e)) (1a, 1b, 1c, 1e and 1f)

A solution of Ru$_3$(CO)$_{12}$ (2 mmol) was refluxed for 4 h in 100 ml of heptane with Fe(CO)$_3$(R-DAB-(4e)) (**1a**, **1b**, **1c**, **1e** or **1f** respectively; 3 mmol) until the ν(CO) pattern of the starting material in the IR spectrum of the reaction mixture was replaced by that of FeRu(CO)$_6$(R-DAB(6e)) (**3a**, **3b**, **3c**, **3e** or **3f**, respectively). During the reaction the colour of the solution changed from deep red to red. The solution was allowed to cool to room temperature and filtered to remove precipitated Ru$_3$(CO)$_{12}$. The solvent was evaporated, the residue was dissolved in 1 ml of CH$_2$Cl$_2$ and the product was separated by column chromatography. The orange first fraction (eluent hexane) contained Ru$_3$(CO)$_{12}$ while the red second fraction (eluent hexane:diethyl ether = 10:1) contained the product **3**. The fractions containing **3** were evaporated to dryness. Crystallization of the crude product from 10 ml of hexane at −20 °C yielded (calculated on **1**) **3a**, 65% (1.95 mmol); **3e**, 50% (1.5 mmol); and **3f** 65% (1.95 mmol) of red crystals. Compound **3b** could not be purified by chromatography and **3c** did not crystallize upon cooling, but their formation was established by IR, ^{1}H NMR and mass spectroscopy of the crude product.

FeRu(CO)$_6$(CH(i-Pr)$_2$-DAB(6e)) (3d) by reaction of Fe$_2$(CO)$_9$ with Ru(CO)$_3$(CH(i-Pr)$_2$-DAB)) (2d)

A solution of Ru(CO)$_3$(CH(i-Pr)$_2$-DAB(4e)) (**2d**) (3 mmol) and Fe$_2$(CO)$_9$ (3 mmol) were refluxed for 24 h in 150 ml of octane, until the ν(CO) pattern of the starting material in the IR spectrum of the reaction mixture was replaced by that of FeRu(CO)$_6$-(CH(i-Pr)$_2$-DAB(6e)) (**3d**). A similar work-up procedure was followed (*vide supra*). However, since **3d** did not crystallize upon cooling its formation was established by IR, ^{1}H NMR and mass spectroscopy of the crude product. Yield (calculated on **2d**) of **3d** 60% (1.8 mmol) of a waxy solid.

FeRu(CO)$_6$(i-Pr-DAB(6e)) (3a) by reaction of Fe$_2$(CO)$_9$ with Ru(CO)$_3$(i-Pr-DAB(4e)) (2a)

A solution of Ru$_3$(CO)$_{12}$ (2 mmol) and i-Pr-DAB (1 mmol) were stirred for 20 min in 150 ml of heptane at 80 °C. The colour of the solution changed to blood red and IR spectroscopy at this stage of the reaction mixture indicated the presence in solution of Ru(CO)$_3$(i-Pr-DAB(4e)) (**2a**) and Ru$_3$(CO)$_{12}$. The solution was cooled to −20 °C to avoid the formation of Ru$_2$(CO)$_6$(i-Pr-DAB(6e)). The excess Ru$_3$(CO)$_{12}$ precipitated and was filtered off. Fe$_2$-(CO)$_9$ (1 mmol) was added and the solution was refluxed for 4 h until the ν(CO) pattern of **2a** was replaced by that of FeRu(CO)$_6$(i-Pr-DAB(6e)) (**3a**). The work-up procedure was similar to that of the reaction of **1a** with Ru$_3$(CO)$_{12}$. Yield of **3a** 50% (0.5 mmol, based on i-Pr-DAB).

Attempted Synthesis of FeOs(CO)$_6$(i-Pr-DAB(6e)) and of RuOs(CO)$_6$(CH(i-Pr)$_2$-DAB(6e))

The compounds Fe(CO)$_3$(i-Pr(DAB(4e)) (**1a**) (1 mmol) and Ru(CO)$_3$(CH(i-Pr)$_2$-DAB(4e)) (**2d**) (1 mmol), respectively, were stirred for 72 h in 100 ml of nonane at 140 °C with Os$_3$(CO)$_{12}$ (1 mmol). IR spectroscopic data indicated that no reaction took place.

Reactivity of FeRu(CO)$_6$(R-DAB(6e)) (3)

(i) Reaction of FeRu(CO)$_6$(R-DAB(6e)) (3a and 3e) with allene

A slow stream of allene was passed for about 1 h through a solution of 233 mg (0.5 mmol) of FeRu-(CO)$_6$(R-DAB(6e)) (**3a** or **3e**) in 150 ml of hexane at 40 °C until IR spectroscopy measurements indicated that the ν(CO) pattern of the starting material was replaced by that of FeRu(CO)$_5$(R-DAB-(4e))(C$_3$H$_4$) (**4a** or **4e**). The colour of the solution changed from red to blue. The solvent was evaporated and the residue was dissolved in 1 ml of CH$_2$Cl$_2$ and was purified by column chromatography. Elution with hexane:diethyl ether = 2:1 yielded a blue fraction that contained the product. The fraction containing the product was evaporated to dryness and crystallization from 10 ml of hexane at −20 °C yielded FeRu(CO)$_5$(i-Pr-DAB(4e))(C$_3$H$_4$) (**4a**) 80% (0.4 mmol) or FeRu(CO)$_5$(*p*-Tol-DAB(4e))(C$_3$H$_4$) (**4e**) 35% (0.18 mmol) as dark blue crystals.

(ii) Reaction of FeRu(CO)$_6$(i-Pr-DAB(6e)) (3a) with RN=C=NR (R = i-Pr)

A solution of 233 mg of **3a** (0.5 mmol) and 62 mg of diisopropylcarbodiimide (0.5 mmol) in 150 ml of nonane was slowly heated (about 1 °C/min) starting from room temperature. Samples for IR spectroscopy were taken at temperature intervals of 10 °C. It was found that **3a** slowly decomposed at 120 °C to unidentified material. No C–C coupling product could be detected.

(iii) Reaction of FeRu(CO)$_6$(i-Pr-DAB(6e)) (3a) with i-Pr-DAB

A solution of 116 mg of **3a** (0.25 mmol) and 35 mg of i-Pr-DAB (0.25 mmol) in 100 ml of nonane was slowly heated (about 1 °C/min) starting from room temperature. Samples for IR spectroscopy were taken at temperature intervals of 10 °C. IR spectroscopy indicated that **3a** decomposed at 120 °C to Fe(CO)$_3$(i-Pr-DAB(4e)) (**1a**) and Ru(CO)$_3$(i-Pr-DAB(4e)) (**2a**). No C–C coupling product could be detected.

(iv) Reaction of FeRu(CO)$_6$(i-Pr-DAB(6e)) (3a) with Ru$_3$(CO)$_{12}$ and Os$_3$(CO)$_{12}$

A solution of 116 mg of **3a** (0.25 mmol) and 160 mg of $Ru_3(CO)_{12}$ (0.25 mmol) or 227 mg of $Os_3(CO)_{12}$ (0.25 mmol), respectively, in 100 ml of nonane was slowly heated (about 1 °C/min) starting from room temperature. Samples for IR spectroscopy were taken at temperature intervals of 10 °C. It was found that **3a** slowly decomposed at 120 °C to unidentified products. No $FeRu_2(CO)_9$(R-DAB(8e)) or $FeRuOs(CO)_9$(R-DAB(8e)) could be detected.

(v) Thermolysis of FeRu(CO)$_6$(i-Pr-DAB(6e)) (3a)

A slow nitrogen stream was passed through a solution of 233 mg of **3a** (0.5 mmol) in 150 ml of nonane that was slowly heated (about 1 °C/min) starting from room temperature. Samples for IR spectroscopy were taken at temperature intervals of 10 °C. At 120 °C a weak absorbance appeared in the IR spectrum at 1842 cm^{-1}, possibly due to a semibridging carbonyl belonging to $FeRu(CO)_5$(i-Pr-DAB(8e)).* However, the concentration of the new product remained very low since together with its formation a slow decomposition reaction was observed.

(vi) Thermolysis of FeRu(CO)$_6$(i-Pr-DAB(6e)) (3a) in the presence of CO

The above reaction was performed in a similar way in decane while a slow stream of CO was passed through the solution. Two differences with the above reaction were observed. No absorption at 1842 cm^{-1} was detectable in the IR spectum and **3a** decomposed at 160 °C.

(vii) Reaction of FeRu(CO)$_6$(i-Pr-DAB(6e)) (3a) with Me$_3$NO

Freshly sublimed Me_3NO (38 mg; 0.5 mmol) dissolved in 0.5 ml of CH_2Cl_2 was slowly added to a room temperature solution of 233 mg of **3a** (0.05 mmol) in 150 ml of hexane or alternatively THF. A slow nitrogen stream was passed through the solution. IR spectroscopic data indicated that **3a** decomposed instantaneously.

(viii) Reaction of 3a with Me$_3$NO in the presence of dimethylacetylenedicarboxylate (DMADC); synthesis of FeRu(CO)$_4$(i-Pr-DAB(8e)(DMADC) (5a)

233 mg (0.5 mmol) of **3a** and DMADC in 150 ml of hexane was stirred at 0 °C. IR spectroscopic measurements indicated that no reaction took place. Freshly sublimed Me_3NO (45 mg; 0.6 mmol) dissolved in 1 ml of CH_2Cl_2 was slowly added to this solution. A fast decomposition reaction was observed. Nevertheless the solvent was evporated and the residue could be partly dissolved in 0.5 ml of CH_2Cl_2 and was put on a chromatography column. Elution (hexane:diethylether = 2:1) gave a yellow fraction that was collected. Evaporation of the eluents to 2 ml of and cooling to −80 °C yielded **5a** as small yellow crystals. Yield 3%.

(ix) Reaction of FeRu(CO)$_6$(i-Pr-DAB(6e)) (3a) with Me$_3$NO in the presence of hydrogen

A slow stream of hydrogen gas was passed through a solution of 233 mg (0.5 mmol) of **3a** in 150 ml of hexane at room temperature. IR spectroscopic data indicated that no reaction took place. Freshly sublimed Me_3NO (45 mg; 0.6 mmol) dissolved in 1 ml of CH_2Cl_2 was slowly added to the solution. IR spectroscopic measurements indicated that **3a** decomposed instantaneously.

Crystal Structure Determination of [FeRu(CO)$_6$-(i-Pr-DAB(6e))]; $C_{14}H_{16}FeRuN_2O_6$

Crystals of the title compound are monoclinic, space group $P2_1/a$, with four molecules in a unit cell of dimensions: $a = 22.436(3)$, $b = 8.136(3)$, $c = 10.266(1)$ Å and $\beta = 99.57(1)°$. A total of 5347 independent reflections were measured on a Nonius CAD 4 diffractometer using graphite-monochromated Mo Kα radiation, of which 2302 had intensities below the $2.5\sigma(I)$ level and were treated as unobserved. The metal positions were derived from an E-Fourier obtained by means of the symbolic addition program set SIMPEL [11a]. The remaining non-hydrogen atoms were derived from a subsequent F_o synthesis. After isotropic block-diagonal least-squares refinement ($R = 0.074$) an empirical absorption correction (DIFABS) was applied [11b, c]. Subsequent anisotropic refinement converged to $R = 0.049$ and $R_w = 0.052$ for the 3045 observed reflections. The anomalous dispersion of iron and ruthenium was taken into account and a weighting scheme $\omega = 1/(4.1 + F_o + 0.04F_o^2)^{0.5}$ was applied [11c]. The computer programs were taken from the XRAY-76 system [11d]. The molecular geometry of $FeRu(CO)_6$(i-Pr-DAB(6e)) (**3a**) with the numbering of the atoms is given in Fig. 2, which shows a PLUTO drawing of the molecule [11e]. Atomic parameters, bond lengths and bond angles are given in Tables I, II and III respectively. See also 'Supplementary Material'.

Crystal Structure Determination of [FeRu(CO)$_5$(i-Pr-DAB(4e))(C$_3$H$_4$)]; $C_{16}H_{20}FeRuN_2O_5$

Crystals of the title compound are triclinic, space group $P\bar{1}$, with two molecules in a unit cell of dimensions: $a = 9.7882(7)$, $b = 12.2609(9)$, $c = 8.3343(7)$ Å, $\alpha = 99.77(1)°$, $\beta = 91.47(1)°$ and $\gamma = 86.00(1)°$. A total of 5680 independent reflections were mea-

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*A single-crystal molecular structure determination of $Ru_2(CO)_5$(i-Pr-DAB(8e)) showed that it contains a bridging carbonyl group. The ν(CO) of this carbonyl group appears at 1840 cm^{-1} in the infrared spectrum.

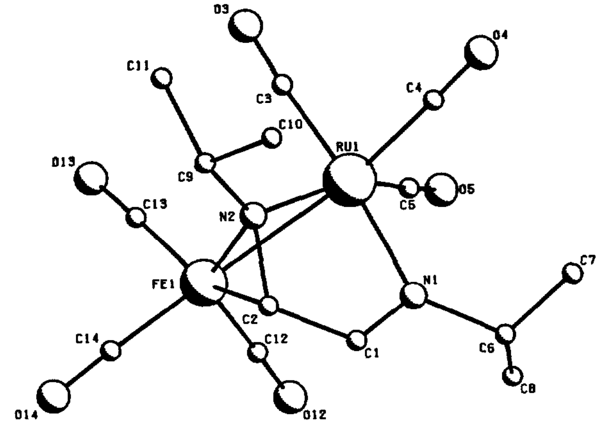


Fig. 2. The molecular geometry of FeRu(CO)$_6$(i-Pr-DAB(6e)) (3a).

TABLE II. Bond Distances (Å) of the Atoms of FeRu(CO)$_6$-(i-Pr-DAB(6e)) (3a)^a

Ru1–Fe1	2.6602(9)	C2–N2	1.414(6)
Ru1–C3	1.892(5)	C3–O3	1.141(7)
Ru1–C4	1.957(5)	C4–O4	1.124(6)
Ru1–C5	1.920(5)	C5–O5	1.135(7)
Ru1–N1	2.138(4)	C6–C7	1.48(1)
Ru1–N2	2.102(3)	C6–C8	1.532(10)
Fe1–C2	2.070(5)	C6–N1	1.501(8)
Fe1–C12	1.783(5)	C9–C10	1.532(8)
Fe1–C13	1.776(5)	C9–C11	1.544(8)
Fe1–C14	1.791(5)	C9–N2	1.488(5)
Fe1–N2	1.942(3)	C12–O12	1.154(6)
C1–C2	1.437(7)	C13–O13	1.163(6)
C1–N1	1.296(6)	C14–O14	1.145(6)

^{a}e.s.d.s given in parentheses.

sured on a Nonius CAD 4 diffractometer using graphite-monochromated Mo Kα radiation, of which 1082 had intensities below the $2\sigma(I)$ level and were treated as unobserved. The metal positions were derived from an E^2 Patterson synthesis. A subsequent F_o synthesis revealed the remaining non-hydrogen atoms. After isotropic block-diagonal least-squares refinement an empirical absorption correction (DIFABS) was applied [11b, c]. Subsequent anisotropic refinement converged to $R = 0.028$ and $R_w = 0.043$ for the 4598 observed reflections. The anomalous dispersion of iron and ruthenium was taken into account and a weighting scheme $\omega = 1/(4.1 + F_o + 0.04F_o^2)$ was applied [11c]. The computer programs were from the XRAY-76 system [11d]. The molecular geometry of FeRu(CO)$_5$(i-Pr-DAB(4e))(C$_3$H$_4$) with the numbering of the atoms is given in Fig. 3, which shows a PLUTO drawing of the molecule [11e]. Atomic parameters, bond lenghts and bond angles are given in Tables IV, V and VI respectively. See also 'Supplementary Material'.

TABLE I. Fractional Coordinates of the Atoms and Equivalent Isotropic Thermal Parameters of FeRu(CO)$_6$(i-Pr-DAB(6e)) (3a)

Atom	x	y	z	U_{eq}
Ru1	0.14289(2)	0.32317(7)	0.22158(5)	0.0398(2)
Fe1	0.03116(4)	0.3103(1)	0.27623(8)	0.0368(4)
C1	0.0868(3)	0.0076(8)	0.2093(7)	0.051(4)
C2	0.0708(3)	0.0840(8)	0.3249(6)	0.046(4)
C3	0.1512(3)	0.5374(9)	0.2939(8)	0.055(4)
C4	0.2293(3)	0.2735(9)	0.2629(7)	0.053(4)
C5	0.1408(3)	0.425(1)	0.0522(7)	0.062(5)
C6	0.1391(4)	−0.009(1)	0.0265(9)	0.088(7)
C7	0.2056(5)	−0.027(2)	0.041(1)	0.17(1)
C8	0.1040(6)	0.065(1)	−0.1007(9)	0.113(9)
C9	0.1247(3)	0.2189(9)	0.5232(6)	0.053(4)
C10	0.1798(4)	0.106(1)	0.5556(8)	0.072(5)
C11	0.1401(4)	0.394(1)	0.5762(7)	0.076(5)
C12	0.0026(3)	0.3056(9)	0.1035(6)	0.051(4)
C13	0.0210(3)	0.5224(9)	0.3069(6)	0.049(4)
C14	−0.0341(3)	0.2533(9)	0.3453(7)	0.053(4)
N1	0.1233(3)	0.0820(7)	0.1433(5)	0.052(3)
N2	0.1050(2)	0.2218(6)	0.3775(5)	0.039(3)
O3	0.1580(3)	0.6688(7)	0.3324(6)	0.083(4)
O4	0.2790(2)	0.2460(8)	0.2874(7)	0.087(4)
O5	0.1390(3)	0.4920(9)	−0.0453(6)	0.094(5)
O12	−0.0169(2)	0.3031(7)	−0.0078(5)	0.070(3)
O13	0.0113(3)	0.6607(7)	0.3230(5)	0.074(4)
O14	−0.0757(2)	0.2113(8)	0.3875(6)	0.081(4)

TABLE III. Bond Angles (°) of the Atoms of FeRu(CO)$_6$-(i-Pr-DAB(6e)) (3a)[a]

Fe1–Ru1–C3	89.3(2)	C13–Fe1–N2	112.9(3)
Fe1–Ru1–C4	151.7(1)	C14–Fe1–N2	111.9(3)
Fe1–Ru1–C5	109.0(2)	C2–C1–N1	119.7(5)
Fe1–Ru1–N1	84.3(2)	Fe1–C2–C1	110.0(4)
Fe1–Ru1–N2	46.3(1)	Fe1–C2–N2	64.6(4)
C3–Ru1–C4	94.3(3)	C1–C2–N2	117.7(5)
C3–Ru1–C5	86.8(4)	Ru1–C3–O3	176.3(4)
C3–Ru1–N1	173.6(2)	Ru1–C4–O4	179.4(4)
C3–Ru1–N2	95.1(3)	Ru1–C5–O5	176.8(4)
C4–Ru1–C5	99.2(3)	C7–C6–C8	119.4(8)
C4–Ru1–N1	91.5(3)	C7–C6–N1	109.6(8)
C4–Ru1–N2	105.4(3)	C8–C6–N1	109.3(7)
C5–Ru1–N1	94.8(3)	C10–C9–C11	110.6(6)
C5–Ru1–N2	155.1(2)	C10–C9–N2	108.8(5)
N1–Ru1–N2	80.9(2)	C11–C9–N2	110.6(5)
Ru1–Fe1–C2	72.8(2)	Fe1–C12–O12	178.8(3)
Ru1–Fe1–C12	89.2(2)	Fe1–C13–O13	176.4(4)
Ru1–Fe1–C13	98.8(2)	Fe1–C14–O14	177.5(4)
Ru1–Fe1–C14	162.7(2)	Ru1–N1–C1	109.9(4)
Ru1–Fe1–N2	51.5(1)	Ru1–N1–C6	133.8(4)
C2–Fe1–C12	106.9(3)	C1–N1–C6	116.2(6)
C2–Fe1–C13	152.2(2)	Ru1–N2–Fe1	82.2(2)
C2–Fe1–C14	91.2(3)	Ru1–N2–C2	106.4(3)
C2–Fe1–N2	41.1(2)	Ru1–N2–C9	133.0(3)
C12–Fe1–C13	99.3(3)	Fe1–N2–C2	74.3(4)

(continued)

TABLE III. *(continued)*

C12–Fe1–C14	101.9(3)	Fe1–N2–C9	128.9(3)
C12–Fe1–N2	131.2(2)	C2–N2–C9	115.0(4)
C13–Fe1–C14	92.5(3)		

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

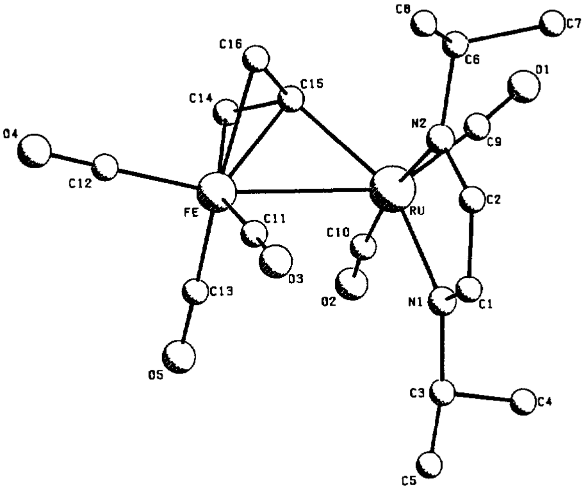


Fig. 3. The molecular geometry of FeRu(CO)$_5$(i-Pr-DAB-(4e))(C$_3$H$_4$) (4a).

TABLE IV. Fractional Coordinates of the Atoms and Equivalent Isotropic Thermal Parameters of FeRu(CO)$_5$(i-Pr-DAB(4e))-(C$_3$H$_4$) (4a)

Atom	x	y	z	U_{eq}
Ru	0.20635(2)	0.23939(2)	0.37679(2)	0.0387(1)
Fe	0.36775(4)	0.27941(4)	0.13203(5)	0.0478(2)
C1	0.0398(3)	0.0644(2)	0.2204(3)	0.046(1)
C2	−0.0410(3)	0.1646(2)	0.2079(4)	0.047(1)
C3	0.2383(3)	−0.0261(2)	0.3337(4)	0.052(1)
C4	0.2060(5)	−0.0481(4)	0.4990(6)	0.094(3)
C5	0.2275(7)	−0.1258(4)	0.2029(7)	0.118(4)
C6	−0.0813(3)	0.3612(2)	0.2804(4)	0.055(2)
C7	−0.1901(4)	0.3614(3)	0.4095(6)	0.077(2)
C8	−0.1458(5)	0.3765(3)	0.1167(6)	0.081(3)
C9	0.1376(3)	0.3032(3)	0.5820(4)	0.054(2)
C10	0.3698(3)	0.2005(3)	0.4796(4)	0.060(2)
C11	0.2514(3)	0.1954(3)	0.0086(4)	0.054(2)
C12	0.4500(4)	0.3355(3)	−0.0216(5)	0.068(2)
C13	0.4998(4)	0.1768(3)	0.1596(5)	0.067(2)
C14	0.4269(3)	0.3978(3)	0.3414(4)	0.061(2)
C15	0.2851(3)	0.3804(2)	0.3188(4)	0.049(1)
C16	0.2295(4)	0.4223(3)	0.1809(4)	0.060(2)
N1	0.1530(2)	0.0748(2)	0.3039(3)	0.041(1)
N2	0.0105(2)	0.2579(2)	0.2678(3)	0.042(1)
O9	0.1031(4)	0.3468(3)	0.7084(3)	0.088(2)
O10	0.4643(3)	0.1731(3)	0.5501(4)	0.089(2)
O11	0.1792(3)	0.1406(3)	−0.0736(3)	0.079(2)
O12	0.4986(4)	0.3706(3)	−0.1229(4)	0.108(3)
O13	0.5867(4)	0.1112(3)	0.1733(5)	0.109(3)

TABLE V. Bond Distances (Å) of the Atoms of $FeRu(CO)_5$-(i-Pr-DAB(4e))(C_3H_4) (4a)^a

Ru–Fe	2.7405(7)	C2–N2	1.298(3)
Ru–C9	1.876(2)	C3–C4	1.493(4)
Ru–C10	1.867(2)	C3–C5	1.502(5)
Ru–C15	2.075(2)	C3–N1	1.496(3)
Ru–N1	2.105(2)	C6–C7	1.533(4)
Ru–N2	2.115(2)	C6–C8	1.524(4)
Fe–C11	1.778(2)	C6–N2	1.490(3)
Fe–C12	1.786(3)	C9–O9	1.145(3)
Fe–C13	1.778(3)	C10–O10	1.143(3)
Fe–C14	2.166(3)	C11–O11	1.143(3)
Fe–C15	1.970(2)	C12–O12	1.138(4)
Fe–C16	2.127(3)	C13–O13	1.146(4)
C1–C2	1.432(3)	C14–C15	1.421(3)
C1–N1	1.296(3)	C15–C16	1.418(3)

^{a}e.s.d.s given in parentheses.

TABLE VI. Bond Angles (°) of the Atoms of $FeRu(CO)_5$(i-Pr-DAB(4e))(C_3H_4) (4a)^a

Fe–Ru–C9	142.51(8)	C13–Fe–C16	160.7(1)
Fe–Ru–C10	86.0(1)	C14–Fe–C15	39.8(1)
Fe–Ru–C15	45.76(7)	C14–Fe–C16	66.5(1)
Fe–Ru–N1	104.73(7)	C15–Fe–C16	40.3(1)
Fe–Ru–N2	100.08(7)	C2–C1–N1	116.5(2)
C9–Ru–C10	88.5(2)	C1–C2–N2	117.7(2)
C9–Ru–C15	97.5(1)	C4–C3–C5	113.0(3)
C9–Ru–N1	112.7(1)	C4–C3–N1	108.2(3)
C9–Ru–N2	91.1(1)	C5–C3–N1	114.7(3)
C10–Ru–C15	91.9(2)	C7–C6–C8	111.7(3)
C10–Ru–N1	94.7(1)	C7–C6–N2	109.8(3)
C10–Ru–N2	170.4(1)	C8–C6–N2	112.1(3)
C15–Ru–N1	149.2(1)	Ru–C9–O9	175.3(2)
C15–Ru–N2	97.7(1)	Ru–C10–O10	174.9(2)
N1–Ru–N2	76.7(1)	Fe–C11–O11	178.2(2)
Ru–Fe–C11	82.4(1)	Fe–C12–O12	177.7(2)
Ru–Fe–C12	166.7(1)	Fe–C13–O13	178.0(2)
Ru–Fe–C13	95.5(1)	Fe–C14–C15	62.6(2)
Ru–Fe–C14	76.0(1)	Ru–C15–Fe	85.3(1)
Ru–Fe–C15	48.97(8)	Ru–C15–C14	120.6(2)
Ru–Fe–C16	75.3(1)	Ru–C15–C16	118.0(2)
C11–Fe–C12	99.8(2)	Fe–C15–C14	77.5(2)
C11–Fe–C13	99.9(2)	Fe–C15–C16	75.8(2)
C11–Fe–C14	154.7(1)	C14–C15–C16	111.9(3)
C11–Fe–C15	115.1(1)	Fe–C16–C15	63.9(2)
C11–Fe–C16	95.7(2)	Ru–N1–C1	114.8(2)
C12–Fe–C13	97.1(2)	Ru–N1–C3	125.1(1)
C12–Fe–C14	98.4(2)	C1–N1–C3	120.1(2)
C12–Fe–C15	119.5(2)	Ru–N2–C2	113.9(2)
C12–Fe–C16	91.4(2)	Ru–N2–C6	127.2(1)
C13–Fe–C14	95.1(2)	C2–N2–C6	117.9(2)
C13–Fe–C15	121.4(1)		

^{a}e.s.d.s given in parentheses.

TABLE VII. IR and FD Mass Data

Compound	M^a (calc.)	IR^b
3a^c	466(465)	2072, 2000, 1996, 1988, 1938
3b^c	494(493)	2064, 2004, 1995, 1983, 1939
3c^c	545(545)	2064, 2000, 1997, 1985, 1936
3d	578(578)	2065, 2004, 1997, 1985, 1938
3e		2072, 2008, 1996, 1946
3f	480(479)	2065, 2001, 1996, 1983, 1936
4a	478(478)	2023, 1997, 1966, 1945
4e	574(573)	2031, 2005, 1972, 1954
5a^c	552(551)	2051, 2024, 1982, 1973

^{a}The observed and calculated masses account for the highest peak of the observed and simulated spectra. ^{b}In n-hexane (cm^{-1}). ^{c}IR and FD mass similar to the reported literature values [5c, 7].

Analytical and Spectroscopic Data

The IR data are listed in Table VII. The complexes **3** show ν(CO) spectra which are in agreement with the reported data [5c]. Except for **3e**, the six terminal carbonyl groups give rise to five strong IR absorptions between 2100 and 1900 cm^{-1}. Complex **3e**, containing *p*-Tol-DAB, gives rise to four absorptions. The complexes **4a** and **4e** show four absorptions in the terminal ν(CO) region. The IR spectrum of **5a** is in agreement with the reported spectrum and shows four absorptions in the terminal ν(CO) region (see Table VII) [7].

FD mass spectra have been recorded of all the products, except for **3e** which decomposed. The observed and calculated masses were, within experimental error, the same, see Table VII. The heteronuclear character of the complexes was evidenced by the isotope pattern of the products that agreed well with the calculated isotopic patterns.

Elemental analyses for the new complexes gave satisfactory results (see 'Supplementary Material').

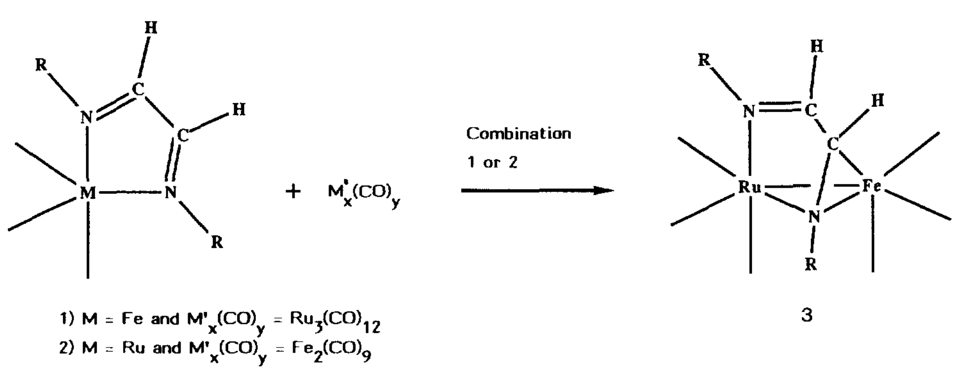
Results and Discussion

Formation and Characterization of $FeRu(CO)_6$R-DAB(6e)) (3)

Formation of $FeRu(CO)_6$(R-DAB(6e)) (3)

The complexes **3** are formed according the reactions in Scheme 1.

The complexes $Fe(CO)_3$(R-DAB(4e)) (**1a**, **1b**, **1c**, **1e** and **1f**) reacted with $Ru_3(CO)_{12}$ in 4 h in refluxing heptane to give $FeRu(CO)_6$(R-DAB(6e)) (**3a**, **3b**, **3c**, **3e** and **3f**). In compound **3** the R-DAB ligand is bonded in the 6e coordination mode: σ-N to Ru, μ_2-N' bridging the Fe–Ru bond and η^2-C=N' to Fe (*vide infra*). In the reaction of $Fe(CO)_3$(i-Pr-DAB; Me, H(4e)) (**1f**), containing an asymmetric i-Pr-DAB-{Me, H} ligand, with $Ru_3(CO)_{12}$ only the complex with the σ-N=C(Me) moiety coordinated to Ru and the η^2-C(H)=N' moiety coordinated to Fe was formed. This was expected since the C(Me)=N part of the ligand is known to be a weaker π-acceptor [5b].



Scheme 1. Formation of $FeRu(CO)_6$(R-DAB; R^1, H(6e)) complexes (**3a**: R = i-Pr, R^1 = H; **3b**: R = t-Bu, R^1 = H; **3c**: R = c–Hex, R^1 = H; **3d**: R = $CH(i\text{-}Pr)_2$, R^1 = H; **3e**: R = p-Tol, R^1 = H; **3f**: R = i-Pr, R^1 = Me).

Complexes **3a** and **3d** could also be prepared by the reaction of $Ru(CO)_3$(R-DAB(4e)) **2a** and **2d** with $Fe_2(CO)_9$. The syntheis of **3a** by the reaction of **2a** with $Fe_2(CO)_9$ (**2a** prepared *in situ* as it cannot be isolated [12]) was performed by refluxing the reaction mixture for 4 h in heptane. However, for the reaction of **2d** with $Fe_2(CO)_9$ 24 h refluxing in octane was necessary to have complete conversion to **3d**. It is of importance to note that in all reactions η^2-C(H)=N coordination to the Fe atom is found (*vide infra*) irrespective of the reaction route performed for the synthesis of **3**.

Similar to the reaction depicted in Scheme 1 the synthesis of heterodinuclear compounds containing an FeOs or RuOs bond was attempted by reacting **1a** and **2d**, respectively, with $Os_3(CO)_{12}$. However, it was found that even at 140 °C neither **1a** nor **2d** reacted with $Os_3(CO)_{12}$ which is probably due to the kinetic stability of $Os_3(CO)_{12}$.

Molecular geometry of $FeRu(CO)_6$(i-Pr-DAB(6e)) (3a)

The molecular geometry of **3a** together with the atomic numbering is given in Fig. 2. In Tables II and III the bond lengths and angles are given. As shown in the Figure the molecule comprises an Fe(1)–Ru(1) bond with a length of 2.6602(9) Å. This value lies in between the value of 2.579(1) Å for the Fe–Fe bond in $Fe_2(CO)_6$(c-Hex-DAB(6e)) [5d] and the value of 2.735(2) Å for the Ru–Ru bond in $Ru_2(CO)_2(\mu\text{-}CO)_2(\eta^5\text{-}C_5H_5)_2$ [13] but is similar to that of 2.626(1) Å in $FeRu(CO)_2(\mu\text{-}CO)_2(\eta^5\text{-}C_5H_5)_2$ [14]. The metal carbonyl part of the molecule consists of three carbonyl groups terminally bonded to iron [Fe–C(O) = 1.783(3) Å (mean)] and three carbonyl groups terminally bonded to ruthenium [Ru–C(O) = 1.923(3) Å (mean)]. The Ru–C(3) bond length of 1.829(5) Å is shortened due to the *trans* influence of N(1).

The 6e donor R-DAB ligand is coordinated to Ru(1) via N(1) and N(2), occupying an apical and an equatorial site respectively, with approximately equal bond lengths: Ru(1)–N(1) = 2.138(4) and Ru(1)–N(2) = 2.102(3) Å. Taking the longer covalent radius of ruthenium with respect to iron into consideration these metal-to-ligand bond distances are analogous to those found in the isostructural complex $Fe_2(CO)_6$(c-Hex-DAB(6e)). The C(2)=N(2) part of the ligand is η^2-coordinated to iron, with C(2) in an apical and N(2) in an equatorial site with slightly different bond lengths: Fe(1)–C(2) = 2.070(5) and Fe(1)–N(2) = 1.942(3) Å. The NCCN part of the ligand, forms together with Ru(1) a five-membered ring which is almost flat, C(2) having the largest deviation from the least-squares plane (0.135 Å).

The imine C(1)=N(1) bond length of the σ-coordinated part of the ligand is 1.296(6) Å. This bond is only slightly elongated as compared to the $C(sp^2)$=$N(sp^2)$ double bond of 1.258(3) in free c-Hex-DAB [15]. However, the η^2-coordinated imine bond C(2)=N(2) is elongated to 1.414(6) Å, which is close to the value of 1.397(4) Å found for the η^2-C(H)=N bonded imine moiety in $Fe(CO)_6$(c-Hex-DAB(6e)). This extensive bond lengthening upon η^2-C=N coordination is explained by π-backbonding from Fe(1) into the π*-orbital of the C=N double bond [4a–c, 16a, b]. The central C(1)–C(2) distance of 1.437(7) Å is normal for a single $C(sp^2)$–$C(sp^2)$ bond and similar to that of 1.457(3) Å found in free c-Hex-DAB. The observation that the R-DAB ligand is σ-N=C coordinated to the Ru atom and η^2-C=N coordinated to the Fe atom indicates that Fe interacts more efficiently with the π-C=N bonds than Ru does.

The question why η^2-C=N coordination to Fe instead of to Ru is preferred is interesting. Several related examples can be referred to, which however, do not give a clear picture of the coordination behaviour of Fe when compared with that of Ru. It has been found that FeRu–carbonyl clusters react with phosphines to give products in which the phosphines are preferentially bonded to the Ru atoms [17a, b]. However, in the synthesis of $FeRu(CO)_6(C_{16}H_{22})$

TABLE VIII. ^1H NMR Data[a]

Compound	R group[b]	Imine H	Allene H
3a[c] (i-Pr-DAB)	0.95(d, 6 Hz, 6H); 1.39(d, 3 Hz), 3H)/1.50(d, 3 Hz, 3H) 2.88(sept, 6 Hz, 1H); 3.11(sept, 6 Hz, 1H)	2.93(d, 2 Hz, 1H) 7.00(d, 2 Hz, 1H)	
3c[c] (c-Hex-DAB)	1–2(br, 20H) 2.36(br-multiplet, 2H)	3.26(d, 2 Hz, 1H) 6.97(d, 2 Hz, 1H)	
3d[d] (CH(i-Pr)$_2$-DAB))	0.57(d, 6 Hz, 3H); 0.61(d, 6 Hz, 3H); 0.72(d, 6 Hz, 3H); 0.80(d, 6 Hz, 3H) 0.88(d, 6 Hz, 3H); 0.95(d, 6 Hz, 3H); 1.09(d, 6 Hz, 3H); 1.18(d, 6 Hz, 3H) 1.37(m, 1H); 1.83(m, 1H); 2.10(m, 1H) 2.25(m, 1H); 2.49(m, 1H); 2.59(m, 1H)	3.09(d, 2 Hz, 1H) 6.93(d, 2 Hz, 1H)	
3e (*p*-Tol-DAB)	1.99(s, 3H)/2.07(s, 3H) 6.78(s, 4H); 6.83(d, 9 Hz, 2H); 7.34(d, 9 Hz, 3H)	3.27(d, 2 Hz, 1H) 7.02(d, 2 Hz, 1H)	
3f (i-Pr-DAB; Me, H)	1.91(s, 3H); 1.04(d, 6 Hz, 3H)/1.09(d, 6 Hz, 3H): 1.46(d, 6 Hz, 6H) 3.26(sept, 6 Hz, 1H)/3.45(sept, 6 Hz, 1H)	3.24(s, 1H)	
4a (i-Pr-DAB)	0.81(d, 6 Hz, 6H); 0.96(d, 6 Hz, 3H)/1.00(d, 6 Hz, 3H) 3.69(sept, 6 Hz, 1H); 4.32(sept, 6 Hz, 1H)	7.05(s, 1H) 7.24(s, 1H)	2.95(d, 1 Hz, 1H); 2.30(d, 1 Hz, 1H) 3.15(dd, 4 Hz, 1H); 4.04(dd, 4 Hz, 1 Hz, 1H)
4e (*p*-Tol-DAB)	1.55(s, 6H) 7.14(s, 4H); 6.95(d, 9 Hz, 2H); 6.82(d, 9 Hz, 2H)	7.25(s, 1H) 7.28(s, 1H)	2.12(s, 1H); 2.73(s, 1H) 3.87(d, 4 Hz, 1H); 3.02(d, 4 Hz, 1H)

[a] The values (ppm relative to TMS) have been obtained in benzene-d_6 solutions at 100 MHz. [b] Vertical bars separate diastereotopic pairs; s = singlet, d = doublet, sept = septet, m = multiplet, br = broad. [c] Similar to the reported literature values [7]. [d] Obtained at 250 MHz.

TABLE IX. ^{13}C NMR Data[a]

Compound	R group	Amine C	Imine C	Ru–CO	Fe–CO	Allene C
3a (i-Pr-DAB)	22.5; 22.6; 26.7; 27.0 60.3; 66.4	64.5	174.7	187.2; 197,4; 204.3	215.9	
3d (CH(i-Pr)$_2$-DAB)	17.6; 17.7; 19.8; 20.5; 21.7; 22.0 22.3; 24.3; 29.3; 30.0 34.1; 37.5; 83.4; 84.9	72.2	174.6	186.4; 197.5; 204.5	215.0	
3e (*p*-Tol-DAB)	20.9 121.1; 124.9; 130.3; 130.4 136.4; 136.6 148.8; 156.4	69.0	172.9	185.9; 197.0; 201.8	215.0	
3f (i-Pr-DAB; Me, H)	15.1; 21.0; 24.8; 26.8; 27.6 53.7; 66.6	69.7	186.0	187.6; 197.4; 205.0	216.3	
4a (i-Pr-DAB)	22.5; 24.0; 25.6; 27.2 60.1; 66.6		149.9 152.9			61.0; 70.5 176.1
4e (*p*-Tol-DAB)	21.1 122.3; 123.6; 130.0; 130.6 138.3; 138.7 149.8; 151.6		149.6 152.7			62.8; 71.3 177.9

[a] The values (ppm relative to TMS) have been obtained in benzene-d$_6$ solutions on a Bruker AC100 spectrometer using an attached proton test pulse sequence. Carbons bearing an even/uneven number of protons gave positive/negative signals.

by the reaction of $Fe(CO)_3(C_{16}H_{22})$ with $Ru_3(CO)_{12}$ or alternatively the reaction of $Ru(CO)_3(C_{16}H_{22})$ with $Fe_3(CO)_{12}$, a product was obtained containing a ruthenacyclo-2,4-pentadiene unit coordinated to Fe [17c]. Contrasting to this it is observed in the synthesis of FeRu(CO)(μ-CO)(μ-CR^{3}CR^{2}CHR^1)(η^5-C$_5$H$_5$)$_2$ (for a whole range of R groups) that a mixture of products is obtained with the alkene moiety bonded to Fe and Ru, respectively [14]. Unfortunately these examples do not give a clear picture of the reason why in some cases coordination of a ligand to Ru is preferred while in other examples the coordination to Fe is preferred or even no preference is observed.

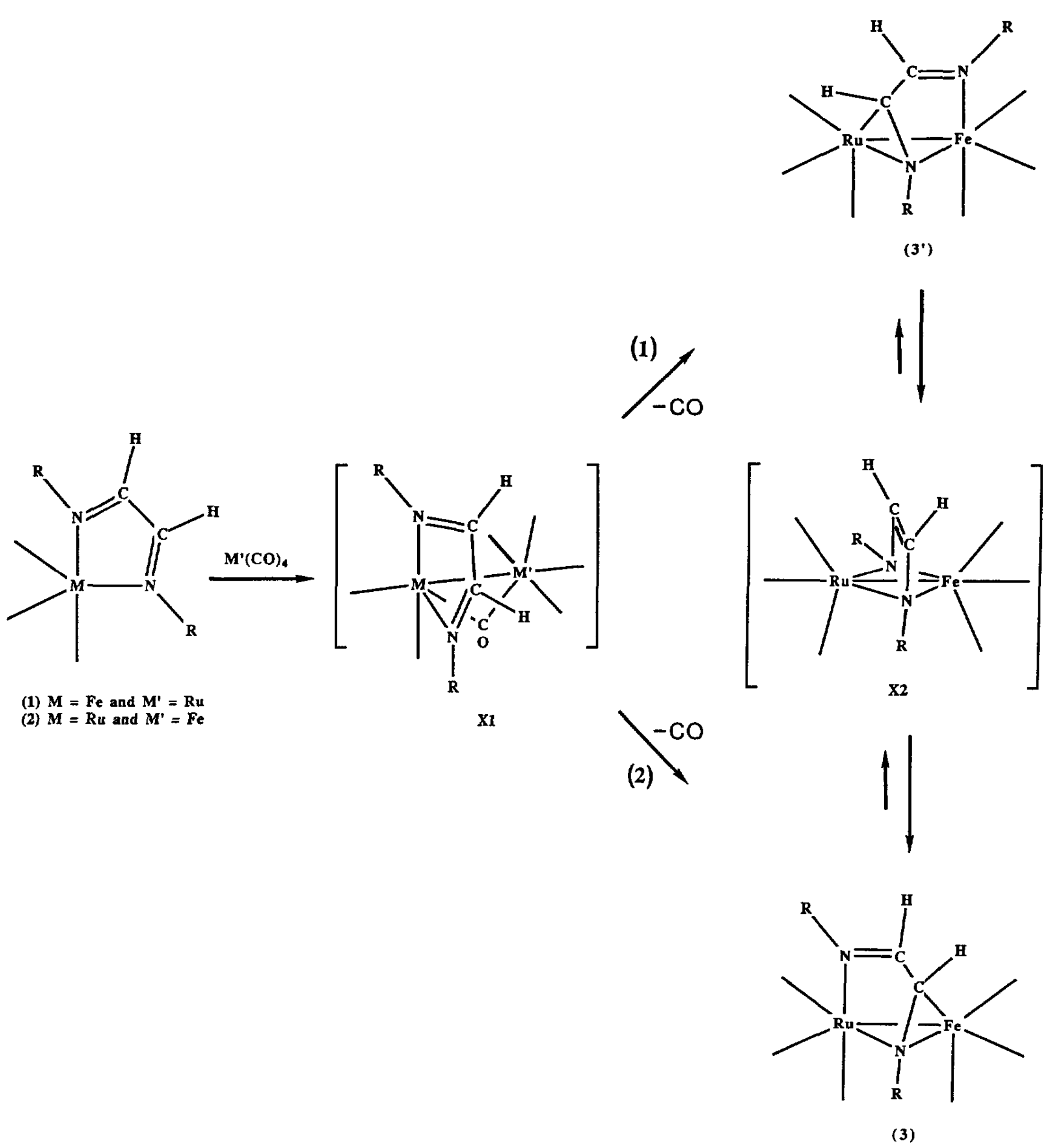
NMR Spectroscopy of compounds 3

The ^{1}H NMR and ^{13}C NMR data are listed in Tables VIII and IX respectively.

In free R-DAB the imine protons and carbon atoms absorb in the 7–9 and 140–175 ppm regions respectively. These positions are hardly affected if only σ-N coordination occurs. However, if R-DAB also uses its π-electrons for coordination, than the resonances of the imine protons and carbon atoms are shifted drastically upfield [4a–c]. For example, in $Fe_2(CO)_6$(R-DAB(6e)) and $Ru_2(CO)_6$(R-DAB(6e)) the imine protons of the σ-N=C(H) coordinated part of the ligand appear at 7.5 ppm while the η^2-C(H)=N protons appear around 3.3 ppm. For the imine carbon atoms these values are 175 and 60 ppm for $Fe_2(CO)_6$(R-DAB(6e)) and 174 and 56 ppm for $Ru_2(CO)_6$(R-DAB(6e)) respectively [18].

For the $FeRu(CO)_6$(R-DAB(6e)) complexes **3** separate signals are found for the two magnetically inequivalent R groups in both the ^{1}H and ^{13}C NMR spectra. For the imine protons chemical shifts of 7 and 3.3 ppm are found for the σ-N=C(H) and η^2-C(H)=N coordinated moieties of the R-DAB ligand respectively. These values are comparable to those observed for the $M_2(CO)_6$(R-DAB(6e)) (M = Fe, Ru) complexes. Interestingly, in the ^{13}C NMR spectra of the complexes **3** the σ-N=C and η^2-C=N coordinated imine carbon atoms absorb around 174 and 69 ppm respectively. The latter value is significantly downfield from the values found for $Ru_2(CO)_6$(R-DAB(6e)) and even for $Fe_2(CO)_6$(R-DAB(6e)). When these values are interpreted in terms of η^2-C=N–metal interactions this would point to a deshielding effect for the η^2-C=N coordinated imine carbon atom in the $FeRu(CO)_6$(R-DAB(6e)) complexes **3**, compared to the $M_2(CO)_6$(R-DAB(6e)) (M = Fe, Ru) complexes, caused by either stronger σ-interactions and/or weaker π-interactions of the Fe atom in $FeRu(CO)_6$(R-DAB(6e)) with the η^2-C=N coordinated imine moiety.

For complex **3f** in principle two isomers can be formed; an isomer with the C(H)=N or the C(Me)=N part of the R-DAB ligand η^2-coordinated. However, the resonance at 3.24 for the imine proton and 69.7 ppm for the imine C(H) carbon shows that only the isomer with the C(H)=N part of the ligand η^2-coordinated is formed. This is probably due to a combined effect of steric and electronic influences of the methyl group.



Scheme 2. Proposed mechanism for the formation of $FeRu(CO)_6(R\text{-}DAB(6e))$ (3).

Variable temperature NMR experiments up to 140 °C for **3a** and up to 100 °C for **3f**, containing 6e bonded i-Pr-DAB{H, H} and i-Pr-DAB{Me, H} ligands respectively, showed no fluxional behaviour of the α-diimine ligands. Also in the $M_2(CO)_6(R\text{-}DAB(6e))$ (M = Fe, Ru) complexes no fluxionality of the R-DAB ligands was observed. It should be noted, however, that fluxionality of the R-DAB ligands cannot be excluded because it was observed in $MnCo(CO)_6$(c-Pr-DAB{Me, Me}) and CpRuCo-$(CO)_3$(i-Pr-DAB(6e)) [16a, 19a]. The absence of fluxionality in the case of **3f** may be compared with the rigid coordination of 1,1-dimethylallene ligand in $[(1,1\text{-dimethylallene})PtCl_2]_2$ for which it was found that the coordination of the $C{=}CH_2$ moiety is favoured to coordination of the $C{=}CMe_2$ moiety of the allene ligand to the Pt atom [19b].

Possible mechanism for the formation of FeRu-(CO)$_6$(R-DAB(6e)) (3)

For the formation of **3** we wish to refer to the work of Frühauf *et al.* who investigated the formation of $Fe_2(CO)_7$(bipy) and $Fe_2(CO)_6(R\text{-}DAB(6e))$ [20a, b]. Considering these results we propose the same reaction sequence for the reactions of $Fe(CO)_3$-R-DAB(4e)) (**1**) with $Ru_3(CO)_{12}$ and of $Ru(CO)_3$(R-

DAB(4e)) (2) with $Fe_2(CO)_9$, which is depicted in Scheme 2.

The first step in this sequence is the formation of the intermediate $FeRu(CO)_7$(R-DAB(4e)) (**X1**) containing a chelating R-DAB ligand and an Fe–Ru bond bridged by a carbonyl ligand. This assumption is underscored by the observation that the reaction of $Fe(CO)_3$(bipy(4e)) with $Fe_2(CO)_9$ gave $Fe_2(CO)_7$(bipy(4e)), which has the structure of the intermediate **X1**, and which is stabilized by the inability of the bipyridyl ligand to act as a 6e donor. Also in the reaction of $Fe(CO)_3$(R-DAB(4e)) (**1**) with $Fe_2(CO)_9$, $Fe_2(CO)_7$(R-DAB(4e)) is proposed as a first intermediate. The intermediate **X1** can then react further by substituting one carbonyl ligand on Fe (or Ru) by an η^2-coordinated imine moiety resulting in the formation of **3** (or **3'** with the imine moiety η^2-coordinated to Ru, *vide infra*). Examples of the conversion of the 4e to the 6e coordination mode are at hand: e.g. the thermal reaction of $MnCo(CO)_7$(R-DAB(4e)) to $MnCo(CO)_6$(R-DAB(6e)) and the photochemically induced reaction of $Mn_2(CO)_8$(R-DAB(4e)) to $Mn_2(CO)_7$(R-DAB(6e)) [16a, 21].

An intriguing observation is that the reaction of **1** with $Ru_3(CO)_{12}$ and of **2** with $Fe_2(CO)_9$ afforded the same product, *i.e.* the product with the imine moiety of the R-DAB ligand η^2-C=N coordinated to Fe. It seems logical to assume that the reaction of **1** with $Ru_3(CO)_{12}$ first gives **3'** with the imine bond η^2-coordinated to Ru (Scheme 2), which then rearranges to **3** which is apparently the thermodynamically more stable product. For the rearrangement of **3'** to **3** a mechanism might be operating as depicted in Scheme 2. As shown in the Scheme **3'** rearranges to an intermediate **X2** in which the R-DAB ligand is symmetrically bridging the Fe–Ru bond. Subsequently **X2** can rearrange back to **3'** or to **3**, the latter being the more stable isomer. The proposed mechanism is well documented by Frühauf *et al.* and is shown to operate in the photochemical rearrangement of $Fe_2(CO)_5(P(OMe)_3)$(R-DAB(6e)) [22].

Reactivity of FeRu(CO)$_6$(R-DAB(6e)) (3)

In the past the reactivity of $Fe_2(CO)_6$(R-DAB(6e)) and $Ru_2(CO)_6$(R-DAB(6e)) has been investigated extensively [4a–c, 5a–b, 7, 23a–c]. It was therefore of interest to carry out reactions involving **3** as the starting product for comparison with the analogous reactions of the homodinuclear complexes $Fe_2(CO)_6$(R-DAB(6e)) and $Ru_2(CO)_6$(R-DAB(6e)). Part of the results of the studies with $Ru_2(CO)_6$(R-DAB(6e)) are depicted in Scheme 3. The analogous reactions with $Fe_2(CO)_6$(R-DAB(6e)) as starting material, for which in most cases decomposition was observed, will be mentioned in the text.

Our investigations showed that the rich and varied chemistry that was observed for $Ru_2(CO)_6$(R-DAB(6e)) (Scheme 3) is absent for **3a**.

Formation and Characterization of FeRu(CO)$_5$(R-DAB(4e))(C$_3$H$_4$)

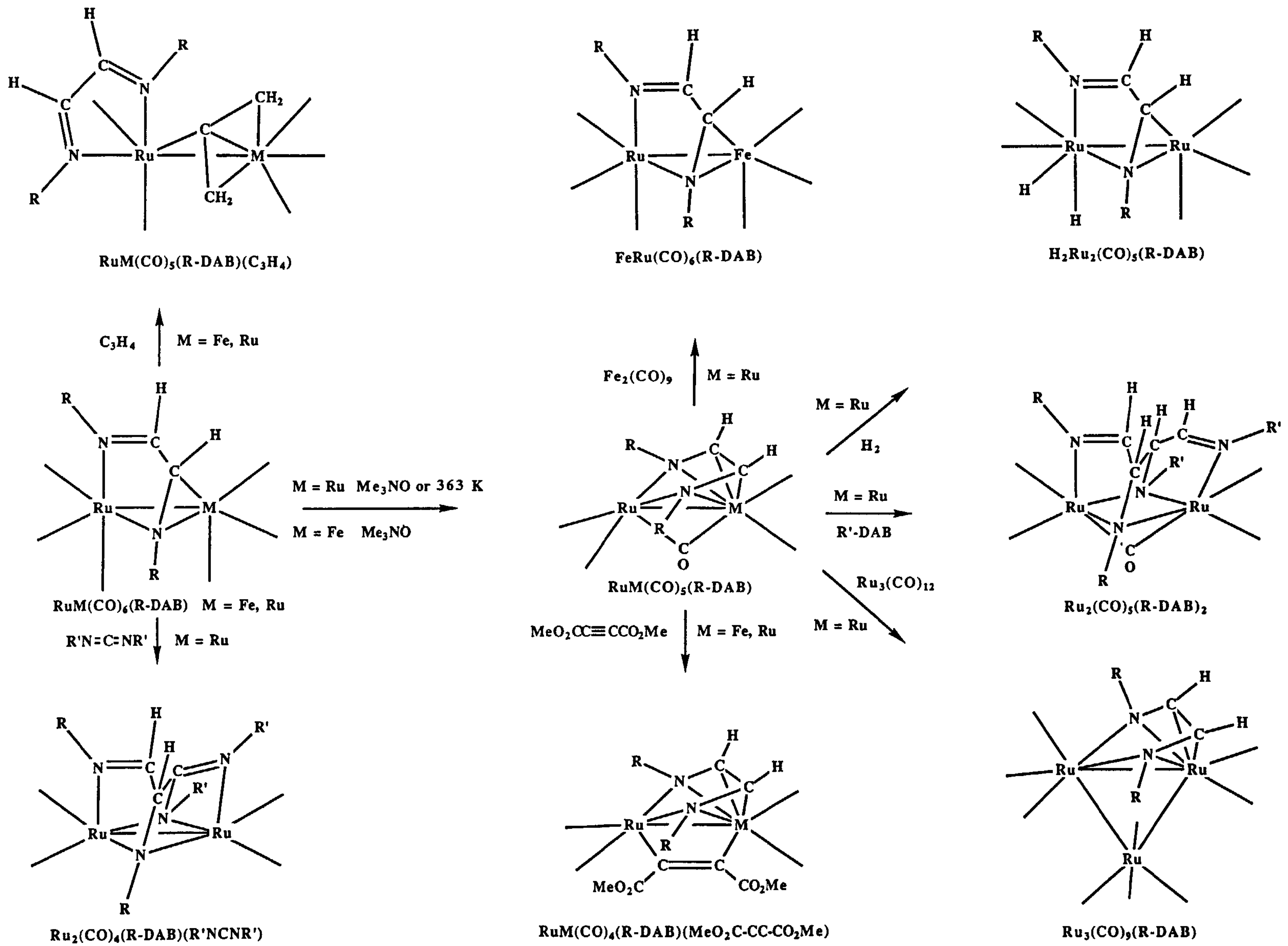
It was found that $FeRu(CO)_6$(R-DAB(6e)) (**3a** and **3e**) reacted with allene at 40 °C to give $FeRu(CO)_5$(R-DAB(4e)(C_3H_4) (**4a** and **4e**).

The molecular geometry of **4a** was established by an X-ray structure determination and is given in Fig. 3. In Tables V and VI the bond lengths and angles are given. The figure shows that starting from **3a** the η^2-coordinated imine function and a carbonyl have been substituted by a bridging 4e donating allene molecule. The Fe–Ru bond, which is still present, has a bond length of 2.7405(7) Å which is longer than that of 2.6602(9) Å in **3a** and 2.626(1) Å in $FeRu(CO)_2(\mu\text{-}CO)_2(\eta^5\text{-}C_5H_5)_2$. The molecule contains five terminal carbonyl ligands, two of which are coordinated to Ru [Ru–C(O) = 1.872(1) Å (mean)] and three coordinated to Fe [Fe–C(O) = 1.781(2) Å (mean)].

The allene ligand is coordinated approximately perpendicular to the Fe–Ru bond. The three C atoms are coordinated to Fe in an allylic fashion, the Fe–C(15) bond of 1.970(2) Å being shorter than the Fe–C(14) and Fe–C(16) bonds of 2.166(3) and 2.127(3) Å respectively. The central carbon of the allene molecule is σ-coordinated to Ru with a Ru–C(15) bond length of 2.075(2) Å. Due to the larger covalent radius of ruthenium compared to iron the Ru–C(15) bond is longer than the Fe–C(15) bond. The C(14)–C(15) and C(15)–C(16) distances of 1.421(3) and 1.418(3) Å, respectively, are in agreement with a weakening of the C–C bonding upon coordination of the allene molecule. A similar coordination of an allene ligand is found in for example $Os_3(CO)_{11}(C_3H_4)$ [24].

The α-diimine ligand is chelate coordinated to ruthenium with a N(1)–Ru–N(2) bite angle of 76.7(1)°. Similar angles are found in many other compounds with chelating R-DAB ligands. For example, in $ReBr(CO)_3$(R-DAB(4e)) and $Os_3(CO)_{10}$(i-Pr-DAB(4e)) bite angles of 72.7(7)° and 76.6(7)°, respectively, are observed [25a, b]. The five-membered ring formed by the chelating ligand and ruthenium is almost flat. The largest deviation from the least-squares plane involves C(1) which lies 0.042 Å out of this plane. The Ru–N(1) of 2.105(2) Å and the Ru–N(2) of 2.115(2) Å are approximately equal. The imine bond lengths of 1.296(3) Å for C(1)=N(1) and 1.298(3) Å for C(2)=N(2) are slightly elongated as compared to the imine bond length of 1.258(3) Å of free c-Hex-DAB. The central C(1)–C(2) bond has a normal sp^2–sp^2 single bond length of 1.432(3) Å.

The NMR data of **4a** and **4e** are in accord with the structure as found in the solid state. Two NMR resonances around 7 ppm are found for the imine protons and around 150 ppm for the imine carbon atoms showing that the diimine ligand is bonded in



Scheme 3. Comparison of the reactivity of $Ru_2(CO)_6$(R-DAB(6e)) and $FeRu(CO)_6$(i-Pr-DAB(6e)) (3a).

a chelating 4e donating fashion. Separate NMR signals are found for the two R groups of the R-DAB ligand, for the allene CH_2 carbon atoms and for all allene protons. In the case of **4a** the i-Pr methyl groups are diastereotopic. The central carbon atoms of the allene ligand absorb at 176 ppm. The observation of separate signals for the two halves of the R-DAB ligand and the allene ligand in the NMR indicates that the asymmetry of the complex as observed in the solid state for **4a**, is clearly retained in solution.

The reaction of $FeRu(CO)_6$(R-DAB(6e)) (**3a** and **3e**) with allene is comparable to the reactions of $Fe_2(CO)_6$(R-DAB(6e)) and $Ru_2(CO)_6$(R-DAB(6e)) with allene which were found to give the isostructural homonuclear products: $Ru_2(CO)_5$(R-DAB(4e))(C_3H_4) and $Fe_2(CO)_5$(R-DAB(4e))(C_3H_4) [26]. This indicates that both the η^2-coordinated imine function to iron and to ruthenium can be easily substituted by allene.

Comparison of the reactivity of 3a with that of $M_2(CO)_6$(R-DAB(6e)) (M = Fe, Ru)

It is known that $Ru_2(CO)_6$(R-DAB(6e)) reacts with diisopropylcarbodiimide to give a C(imine)–C(carbodiimide) coupled product (Scheme 3) [23a]. Interestingly in the reaction of **3a** with diisopropylcarbodiimide at 120 °C a slow decomposition of **3a** was observed and no C–C coupled products were isolated. This observation for **3a** parallels with the reactivity of $Fe_2(CO)_6$(R-DAB(6e)) with carbodiimides which also gave decomposition. The formation of C–C coupled products with $Ru_2(CO)_6$(R-DAB(6e)) is explained by the susceptibility to electrophilic attack of the imine carbon atom when the C=N bond is η^2-coordinated to Ru which is apparently not the case when the C=N bond is η^2-coordinated to Fe as in **3a** and $Fe_2(CO)_6$(R-DAB).

It has been observed that $Ru_2(CO)_6$(R-DAB(6e)) reacts to $Ru_2(CO)_5$(R-DAB(8e)), containing an 8e coordinated R-DAB ligand and a bridging carbonyl, which is a crucial intermediate for many reactions (see Scheme 3). Therefore we attempted to synthesize $FeRu(CO)_5$(R-DAB(8e)) in which both imine functions should be coordinated to iron. However both the reaction of **3a** with trimethylamine-*N*-oxide at room temperature and the thermolysis of **3a** at 120 °C gave decomposition and not $FeRu(CO)_5$(i-Pr-DAB(8e)). However, the observation of a weak absorbance at 1842 cm^{-1} in the IR spectrum in the latter reaction, which is absent when CO is passed through the solution, might indicate the formation of an $FeRu(CO)_5$(i-Pr-DAB(8e)) complex. Interestingly also $Fe_2(CO)_5$(R-DAB(8e)) could not be isolated. In a search for more indications that a thermally unstable $FeRu(CO)_5$(i-Pr-DAB(8e)) was formed we performed the thermolysis reaction of **3a** and the reaction of **3a** with Me_3NO in the presence of a reactant (*vide infra*). These reactants were found to give stable products when reacted with $Ru_2(CO)_5$(R-DAB(8e)) (see Scheme 3) [5c, 27].

The thermal reaction of **3a** with R-DAB and $Ru_3(CO)_{12}$ at 120 °C, however, gave decomposition of **3a** which contrasts with the reactivity of $Ru_2(CO)_6$(R-DAB(6e)) with these molecules. For the latter compound it was found that as a first step $Ru_2(CO)_6$(R-DAB(6e)) reacted to $Ru_2(CO)_5$(R-DAB(8e)) that subsequently could be reacted further with either R-DAB to a C–C coupled product or with $Ru_3(CO)_{12}$ to $Ru_3(CO)_9$(R-DAB(8e)) (see Scheme 3) [5c, 12, 27]. However, it should be noted that reaction of $Fe_2(CO)_6$(R-DAB(6e)) with R-DAB gave decomposition and no C–C coupled products.

The reaction of **3a** with trimethylamine-*N*-oxide, to generate $FeRu(CO)_5$(R-DAB(8e)), in the presence of molecular hydrogen was also attempted. However, only decomposition was observed. This contrasts with the reactivity of $Ru_2(CO)_5$(R-DAB(8e)) which was found to react with molecular hydrogen to $H_2Ru_2(CO)_5$(R-DAB(6e)) (Scheme 3).*

Interestingly, the reaction of **3a** with trimethylamine-*N*-oxide in the presence of DMADC (dimethylacetylenedicarboxylate) gave the known $FeRu(CO)_4$(i-Pr-DAB(8e))(DMADC) (**5a**) in low yield [7]. This compound contains an 8e donating R-DAB ligand and a μ_2-bridging acetylene which is parallel to the Fe–Ru bond. For $Ru_2(CO)_5$(R-DAB(8e)) it was found that it reacted with several acetylenes by substitution of the bridging carbonyl to $Ru_2(CO)_4$(R-DAB(8e))(RCCR) that is isostructural with **5a** (see Scheme 3). Also when $Fe_2(CO)_6$(R-DAB(6e)) is reacted with acetylenes $Fe_2(CO)_4$(R-DAB(8e))(RCCR) is formed, probably via $Fe_2(CO)_5$(R-DAB(8e)).

These results indicate that **3a** might react to $FeRu(CO)_5$(R-DAB(8e)), which is however unstable and decomposes rapidly.

Concluding Remarks

It has been shown that $Fe(CO)_3$(R-DAB(4e)) (**1**) reacts with $Ru_3(CO)_{12}$ and $Ru(CO)_3$(R-DAB(4e)) (**2**) with $Fe_2(CO)_9$ to give $FeRu(CO)_6$(R-DAB(6e)) (**3**). In the formation of **3** η^2-coordination of one C=N bond to Fe is preferred to η^2-coordination to Ru. Comparison of the reactivity of $FeRu(CO)_6$(R-DAB(6e)) (**3**) with the reactivity of the corresponding

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*However, the reaction of **3a** with molecular hydrogen in refluxing heptane gave $FeRu(CO)_6(\mu,\mu'$-N(i-Pr)CH_2CH_2-N(i-Pr)). This compound contains a formally dianionic bridging diamido-ethane ligand. A thorough investigation of the reaction showed that it is not formed from $FeRu(CO)_5$(R-DAB(8e)). Contrasting to this the reaction of $Fe_2(CO)_6$(R-DAB(6e)) with molecular hydrogen in refluxing heptane gave decomposition. Details of these interesting reactions will be published in a separate paper.

homodinuclear compounds $M_2(CO)_6$(R-DAB(6e)) (M = Fe, Ru) shows interesting analogies but also differences.

In all cases the reactions of MM'$(CO)_6$(R-DAB-(6e)) (M = M' = Fe, Ru; M = Fe, M' = Ru) with an allene involved the substitution of both the η^2-coordinated imine function and a carbonyl ligand to give MM'$(CO)_5$(R-DAB(4e))(C_3H_4) (4). Apparently the η^2-C=N moiety is easily substituted by allene when coordinated to Fe or Ru.

Interestingly in reactions of FeRu$(CO)_6$(R-DAB-(6e)) and $Fe_2(CO)_6$(R-DAB(6e)) with carbodiimides the C(imine)–C(reactant) coupled products, which were observed in reactions of $Ru_2(CO)_6$(R-DAB(6e)) with carbodiimides, were not found. Apparently when the imine function is η^2-coordinated to iron as in both 3 and $Fe_2(CO)_6$(R-DAB(6e)) the imine carbon is not activated for the above mentioned C–C coupling reactions to proceed.

Attempts to prepare FeRu$(CO)_5$(R-DAB(8e)), that could be a kinetically more active species, analogous to highly reactive homodinuclear compound $Ru_2(CO)_5$(R-DAB(8e)), by reaction of 3 with trimethyl-*N*-oxide or by thermolysis, failed. Interestingly also $Fe_2(CO)_5$(R-DAB(8e)) could not be prepared. It seems that complexes with R-DAB in an 8e coordination mode involving η^2-coordination of both imine functions to iron are unstable. However, when an acetylene moiety is bridging the metal–metal bond this bonding mode is stable since $Fe_2(CO)_4$(R-DAB(8e))(RCCR) and FeRu$(CO)_4$(R-DAB(8e))(RCCR) have shown to be isolable [23c].

Supplementary Material

Listings of elemental analysis data of the new complexes and listings of anisotropic thermal parameters, observed and calculated structure factors of **3a** and **4a** are available from the authors on request.

Acknowledgments

We thank Mr J. M. Ernsting for his assistance with the recording of the NMR spectra and Mrs E. Kluft and Mr G. U. A. Sai for recording the mass spectra. Dr C. J. Elsevier and Dr H. W. Frühauf are thanked for fruitful discussions. We thank the Netherlands Foundation for Chemical Research (S.O.N.) and the Netherlands Organization For Pure Research (Z.W.O.) for their financial support.

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