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Influence of Heteronuclearity on the Dimerization of $HFeRu(CO)_5\{RC{=}C(H)C(H){=}N\text{-}iPr\}$ and the Synthesis of Heterotetranuclear Chain Complexes[1]

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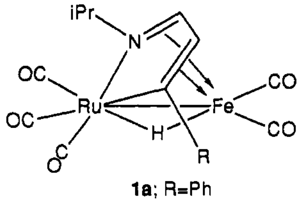
The directed synthesis of heterodinuclear Fe–Ru and of heterotetranuclear Fe_mRu_n ($m = 1$, 2; $n = 4 - m$) chain complexes is described. The thermal reaction of $HFeRu(CO)_5\{RC{=}C(H)C(H){=}N\text{-}iPr\}$ (**1a**, R = Ph; **1b**, R = Me) leads to decomposition in the case of **1b** and to C–H activation within the N-iPr group of **1a**, affording $FeRu(CO)_6\{PhCC(H)C(H)N{=}C(Me)_2\}$ (**2**) and $FeRu_3(CO)_{10}\{PhC{=}C(H)C(H){=}N\text{-}iPr\}_2$ (**3**) as a byproduct. When styrene is used as an additive in this reaction, **2** is formed selectively. When styrene is applied in the thermal reaction of **1b**, smooth conversion into the heterotetranuclear chain complex $Fe_2Ru_2(CO)_{10}\{MeC{=}C(H)C(H){=}N\text{-}iPr\}_2$ (**5**) takes place. Complex **5** is formed as a mixture of four noninterconverting isomers (at 293 K on the NMR time scale), which are assigned on the basis of ^1H and ^{13}C NMR spectra as the *cis* and *trans* isomers of two diastereomers. The expected product of the reaction of **1b** with styrene, i.e. $FeRu(CO)_6\{C(H)_2CC(H)C(H){=}N\text{-}iPr\}$ (**7**), is shown to be formed by the conversion of $[FeRu(CO)_6\{MeC{=}C(H)C(H){=}N\text{-}iPr\}][BF_4]$ (**6b**) on silica. Complex **7** reacts with H_2 to give **1b**. In the reaction of **1a** with 3,3-dimethyl-1-butene, alkene insertion into the Fe–H bond and a subsequent alkyl shift from Fe to C_β of the monoazadienyl (MAD-yl) ligand occurs. Complex **1a** is shown to be a precatalyst for the homogeneous hydrogenation of styrene and α-methylstyrene. As the remaining organometallic species, $FeRu(CO)_6\{PhCC(H)C(H)N(H)\text{-}iPr\}$ (**9aII**) has been isolated. Besides the Fe_2Ru_2 chain complex **5**, also the chain complex $FeRu_3(CO)_{10}\{PhC{=}C(H)C(H){=}N\text{-}iPr\}\{MeC{=}C(H)C(H){=}N\text{-}iPr\}$ (**8**), containing two differently substituted MAD-yl ligands, is prepared by the reaction of **1a** with $Ru_2(CO)_6\{C(H)_2CC(H)C(H){=}N\text{-}iPr\}$ (**13**). The X-ray crystal structures of **7** and **8** have been determined. Crystals of **7** are triclinic, space group $P\bar{1}$, with $a = 8.533(2)$ Å, $b = 9.125(2)$ Å, $c = 11.082(2)$ Å, $\alpha = 69.74(2)°$, $\beta = 82.48(2)°$, $\gamma = 73.41(2)°$, $V = 775.3(3)$ Å^3, $Z = 2$, and final $R = 0.0224$ for 3207 reflections with $I > 2.5\sigma(I)$ and 212 parameters. Crystals of **8I** are monoclinic, space group $P2_1/n$, with $a = 12.088(2)$ Å, $b = 19.314(3)$ Å, $c = 15.016(2)$ Å, $\beta = 111.48(1)°$, $V = 3262.3(9)$ Å^3, $Z = 4$, and final $R = 0.0377$ for 4953 reflections with $I > 2.5\sigma(I)$ and 422 parameters. The structure of **8** shows the presence of a $FeRu_3$-chain metal skeleton, in which, unexpectedly, the Fe atom is situated at a terminal site.

Introduction

A fascinating aspect of the chemistry of heteronuclear transition-metal complexes is the large effect that each of the constituent metals can exert on the reactivity of the complex. Such effects generally are poorly understood. One of the prerequisites for the study of metal properties in heteronuclear complexes is the presence of a ligand system, by which the often subtle effects can be visualized and monitored. Potentially, the ligand should feature a diverse reactivity, thus being sensitive to the kind of metal core to which it is attached.

As may be concluded from our previous report,[1] we have found an appropriate candidate in the monoazadienyl ligand, which is present in the heteronuclear complex $HFeRu(CO)_5\{RC{=}C(H)C(H){=}N\text{-}iPr\}$ (1; Figure 1).



1a; R=Ph
1b; R=Me

Figure 1. Structure of complex 1.

The ligand system in 1 consists of a monoazadiene, $RCH{=}CHCH{=}NR'$, that is cyclometalated by a Ru-carbonyl fragment, thus resulting in a five-membered metallacycle and a hydride ligand. The metallacycle is η^5-coordinated to a $Fe(CO)_2$ unit, and the hydride is probably bridging the intermetallic bond. The interesting reaction sites in 1 are the hydride ligand and the π bonds of the ruthenazadienyl cycle coordinated to Fe. From the reaction of 1 with CO in comparison with the reactivity of the corresponding homonuclear Ru analogues it has

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[1] Reactions of Monoazadienes with Metal Carbonyl Complexes. 13b. For part 13a see: Beers, O. C. P.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L. *Organometallics*, preceding paper in this issue. For earlier parts see refs 2–4, 16, 18, 19, 21, 23, and 28.

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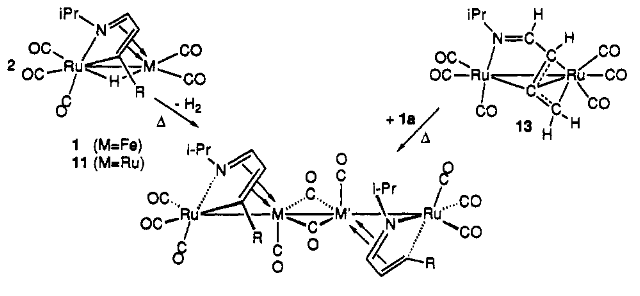

i. Complex 12 (M = M' = Ru), yield 90 % [2].
ii. Intended strategy for M = M' = Fe.
iii. Intended strategy for M = Fe, M' = Ru.

Figure 2. Formation of complex 12 (i) and the intended strategy for the synthesis of heterotetranuclear chain complexes (ii, iii).

appeared that η^2(C=N) and η^2(C=C) coordination to Fe is much stronger than to Ru. Moreover, a great influence of substituents R, attached to the metalated carbon atom of the ligand, was noticed, indicating that the reactivity of the ligand system can be directed by the R group. Therefore, the monoazadienyl ligand appeared to be indeed a suitable ligand system for the examination of metal properties in heteronuclear complexes.

In the present paper we describe the use of complex 1 as a building block for the systematic buildup of heterotetranuclear complexes. Previously, we have shown for the homonuclear system that a linear tetranuclear chain was formed by the thermal dimerization of HRu$_2$(CO)$_5$-{RC=C(H)C(H)=N-iPr} (11) with concomitant loss of H$_2$ (Figure 2).[2] Now we report upon the thermal reaction of the heteronuclear complex 1, where an analogous dimerization is intended, as visualized in Figure 2.

The effect of potentially hydrogen accepting substrates, in particular alkenes, on the dimerization has been studied as well. Complex 1 has further been used as a building block for the directed synthesis of FeRu$_3$-chain complexes in the reaction with Ru$_2$(CO)$_6${C(H)$_2$CC(H)C(H)=N-iPr} (13), which contains an unsaturated ligand system (Figure 2). Finally, in relation to the reaction of 1 with alkenes, the capacity of 1 as a homogeneous catalyst in the hydrogenation of alkenes was examined for several alkenes.

Experimental Section

For general experimental apparatus and techniques, see ref 1. The complexes HFeRu(CO)$_5${RC=C(H)C(H)=N-iPr} (1),[3] Ru$_2$(CO)$_6${RC=C(H)C(H)$_2$-N-iPr} (10),[2] Ru$_2$(CO)$_6${C(H)$_2$CC(H)C(H)=N-iPr} (13),[4] and a solution of in situ prepared FeRu(CO)$_6${MeC=C(H)C(H)=N-iPr}$^+$BF$_4^-$ (6b)[1] were prepared according to literature procedures.

Synthesis of FeRu(CO)$_6${PhCC(H)C(H)N=C(Me)$_2$} (2) and FeRu$_3$(CO)$_{10}${PhC=C(H)C(H)=N-iPr}$_2$ (3) by Thermal Reaction of HFeRu(CO)$_5${RC=C(H)C(H)=N-iPr} (1a,b). A solution of 0.14 g of 1a (0.3 mmol) in 20 mL of heptane was stirred at 110 °C. After 16 h the solution had changed from orange to red. Separation of the products by column chromatography on silica, using hexane/dichloromethane (20:1) as the eluent, yielded 57 mg of the yellow-orange, fairly air-stable complex FeRu(CO)$_6${PhCC(H)C(H)N=C(Me)$_2$} (2; 37%).[5] Subsequent elution with hexane/diethyl ether (50:1) provided a dark red band, containing 34 mg of the moderately air sensitive complex FeRu$_3$(CO)$_{10}${PhC=C(H)C(H)=N-iPr}$_2$ (3; 12% yield).[5] Minor amounts of 9aI,II were eluted with hexane/CH$_2$Cl$_2$ (5:1). Anal. Found (calcd) for C$_{18}$H$_{15}$NO$_6$FeRu (2): C, 43.72 (43.58); H, 2.71 (2.62); N, 2.88 (2.82). FD mass: *m/e* 499 (M_r = 499). Anal. Found (calcd) for C$_{34}$H$_{28}$N$_2$O$_{10}$FeRu$_3$ (3): C, 41.39 (41.51); H, 3.04 (2.87); N, 2.95 (2.85). FD mass: *m/e* 985 (M_r = 985). The same reaction with 1b gave primarily decomposition.

Synthesis of 2 by Reaction of 1a and 1b with Styrene or α-Methylstyrene. When a solution of 0.14 g of 1a (0.3 mmol) in 20 mL of heptane was stirred with a 15–20-fold molar excess of styrene or α-methylstyrene for 8 h at 90 °C, complex 2 was obtained as the only product in 60% yield (0.09 g, purification as described above).

Synthesis of FeRu(CO)$_6${PhC(neo-Pe)C(H)C(H)N-iPr} (4) by Reaction of 1a with 3,3-Dimethyl-1-butene. A solution of 0.14 g of 1a (0.3 mmol) in 30 mL of heptane was stirred with an excess of tBuCH=CH$_2$ (0.25 g, 3.0 mmol) in a closed vessel at 100 °C for 16 h. The reaction mixture was purified by column chromatography on silica. Using hexane/CH$_2$Cl$_2$ (20:1) as the eluent, an orange fraction was obtained containing 0.12 g of the moderately air sensitive complex FeRu(CO)$_6${PhC(neo-Pe)C(H)C(H)N-iPr} (4; 70%). Attempts to crystallize 4 failed. Subsequent elution with hexane/diethyl ether (20:1) yielded a small amount of dark red byproduct, which has not been identified. FD mass for C$_{24}$H$_{27}$NO$_6$FeRu (4): *m/e* 582 (M_r = 583).

Synthesis of Fe$_2$Ru$_2$(CO)$_{10}${MeC=C(H)C(H)=N-iPr}$_2$ (5) by Reaction of 1b with Styrene. A solution of 0.20 g of 1b (0.49 mmol) in 30 mL of heptane was stirred with 0.51 g styrene (10 equiv) at 100 °C. After 0.5 h complex 1b had completely disappeared, indicated by the IR spectrum of the reaction mixture. Purification by column chromatography on silica first yielded an orange fraction (eluent hexane/CH$_2$Cl$_2$ (5:1)) containing minor amounts of 9b. Subsequent elution with hexane/diethyl ether (9:1) yielded an orange-brown fraction, containing complex 5. After concentration of the column fraction, complex 5 was crystallized at −80 °C, affording 0.14 g of brown microcrystalline complex 5 (72% yield). Anal. Found (calcd) for C$_{24}$H$_{24}$N$_2$O$_{10}$Fe$_2$Ru$_2$ (5): C, 35.31 (35.40); H, 2.98 (2.97); N, 3.48 (3.44).

Formation of FeRu(CO)$_6${C(H)$_2$CC(H)C(H)=N-iPr} (7). I. A dichloromethane solution of 0.16 g of 6b (0.3 mmol) was transferred to a silica column. Elution with CH$_2$Cl$_2$ did not yield any complexes. Upon subsequent elution with CH$_2$Cl$_2$/THF (9:1) the product, complex 7, was formed on the column. After evaporation of the solvent, 7 could be further purified by chromatography on a second column, using hexane/CH$_2$Cl$_2$ (20:1) as the eluent. The orange complex 7 was obtained in about 40–60% yield (50–80 mg). Orange crystals suitable for X-ray crystallography were grown from a concentrated hexane solution at −80 °C.

II. Complex 7 was also formed in moderate yields (about 30%), when a solution of 6b in CH$_2$Cl$_2$ was treated with H$_2$O and stirred for 0.5 h. The formation of 7 was indicated by IR and ^{1}H NMR spectroscopy. Anal. Found (calcd) for C$_{13}$H$_{11}$NO$_6$FeRu (7): C, 35.94 (35.97); H, 2.66 (2.55); N, 3.06 (3.23). FD mass: *m/e* 435 (M_r = 435).

Synthesis of FeRu$_3$(CO)$_{10}${MeC=C(H)C(H)=N-iPr}{PhC=C(H)C(H)=N-iPr} (8) by Reaction of 1a with 13. A solution of 0.2 g of 1a (0.43 mmol) with 0.61 g of Ru$_2$(CO)$_6${C(H)$_2$CC(H)C(H)=N-iPr} (13; 1.27 mmol) in 40 mL of heptane was stirred at 50 °C for 30 h. The reaction mixture was then chromatographed on silica. With hexane/CH$_2$Cl$_2$ (10:1) as the eluent the excess of complex 13 was removed. With hexane/diethyl ether (10:1) the red complexes 8I and 8II, present in equimolar amounts, were eluted (total yield 0.32 g, 81%). After the volume of the column fraction was concentrated, complex 8II was crystallized selectively by cooling to −80 °C. The better soluble diastereomer 8I, present in the supernatant, was subsequently crystallized at −80 °C after reducing the volume of the

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(5) Yields are not based on the reaction stoichiometry because here this is not clear *a priori* (see Discussion).

solvent again. In this way dark red crystals of **8I**, suitable for X-ray determination, were grown. Anal. Found (calcd) for $C_{29}H_{26}N_2O_{10}FeRu_3$ (**8**): C, 37.72 (37.79); H, 2.91 (2.85); N, 3.11 (3.04). FD mass: *m/e* 924 (M_r = 924).

Reaction of 3, 5, and 7 with H_2 To Give 1. A solution of 87 mg of complex **7** (0.2 mmol) in 20 mL of heptane was stirred under an H_2 atmosphere at 100 °C for 3 h. The reaction mixture was then examined by ^1H NMR, showing the presence of complex **7** and complex **1b** in the molar ratio 1.5:1. Similarly, a solution of 80 mg of complex **5** (0.1 mmol) in 20 mL of heptane was stirred at 100 °C under 1.5 bar of H_2 for 2 h. After purification of the reaction mixture by column chromatography on silica, 45 mg of complex **1b** was obtained (56%).

When a solution of 98 mg of **3** (0.1 mmol) in 20 mL of heptane was stirred at 90 °C under 1.5 bar of H_2, the red color of the starting solution had disappeared after 2.5 h and the orange solution was examined. IR and ^1H NMR spectroscopy revealed the presence of complex **1a** and $H_4Ru_4(CO)_{12}$ (IR 2079 (s), 2064 (vs), 2023 (s) cm^{-1} (lit.[6] 2081 (s), 2067 (vs), 2030 (m), 2024 (s), 2009 (s) cm^{-1}); ^1H NMR −17.8 ppm (lit.[6] −17.9 ppm)) in an approximate molar ratio of 1.5:1.

Hydrogenation Experiments with Complex 1 and Alkenes. A solution of 0.1 mmol of **1** and an about 100-fold molar excess of alkene either in 10 mL of hexane or in neat alkene was stirred under 1.5 bar of H_2 at 50 °C for 16 h. The reaction mixture was examined with $^1H/^{13}C$ NMR, which showed the following results for the specific combinations of alkene/complex.

Styrene/1a. Styrene appeared to be completely converted into ethylbenzene. The remaining organometallic species were purified by column chromatography on silica. Elution with hexane/CH_2Cl_2 (10:1) yielded the yellow complex $FeRu(CO)_6$-{PhCC(H)C(H)N(H)-iPr} (**9aII**; 25 mg, 48%).

α-Methylstyrene/1a. α-Methylstyrene appeared to be converted into cumene in amounts of 15–20%. Purification with column chromatography on silica yielded as the remaining organometallic species complex **9aII** (22 mg, 44%).

Maleic Anhydride/1a. No hydrogenation product was observed. Complex **1a** appeared to be still present.

3,3-Dimethyl-1-butene/1a. No hydrogenation product was observed. Complex **1a** appeared to be still present together with minor amounts of complexes **2**, **4**, and $FeRu(CO)_6${PhC(H)C(H)C(H)N-iPr}.[1]

Styrene/1b. No hydrogenation product was observed. The only observable organometallic species appeared to be complex **5** (55% yield).

Deuteration Experiments with Styrene/α-Methylstyrene and 1a. When a solution of 0.1 mmol of **1a** in neat styrene/α-methylstyrene (an about 100-fold molar excess) was stirred under 1.5 bar of D_2 at 50 °C for 16 h, complex **9aII** was obtained with ca. 100% incorporation of the D label on nitrogen.

Reaction of 9aII with Styrene under a H_2 Atmosphere. A solution of 0.05 g of **9aII** (0.1 mmol) in 10 mL of hexane was stirred with an about 100-fold molar excess of styrene (1.2 g) in a closed tube under 1.5 bar of H_2 at 50 °C. After 16 h the reaction was stopped and the solvent carefully evaporated (−10 °C). Examination of the reaction mixture by ^1H and ^{13}C NMR indicated that no hydrogenation reaction of styrene had occurred. Complex **9aII** appeared to be still present, which was confirmed spectroscopically after removal of the styrene.

Crystal Structure Determination of 7 and 8I. X-ray data were collected at 100 K on an Enraf-Nonius CAD4 diffractometer. Crystal data are collected in Table I. Both structures were solved with standard Patterson and Fourier techniques (SHELXS86[7]) and refined on *F* by full-matrix least-squares techniques. Neutral atom scattering factors were taken from ref 8 and corrected for anomalous dispersion.[9] All calculations were performed with SHELX76[10] and PLATON[11] (geometrical calculations and illustrations) on a MicroVAX-II (**7**) or a DEC-5000 computer (**8**). Final atomic coordinates and equivalent isotropic thermal parameters are listed in Tables II and III.

Table I. Crystal Data and Details of the Structure Determinations of 7 and 8I

	7	**8I**
	Crystal Data	
formula	$C_{13}H_{11}NO_6FeRu$	$C_{29}H_{26}N_2O_{10}FeRu_3$
mol wt	434.15	921.59
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a, Å	8.533(2)	12.088(2)
b, Å	9.125(2)	19.314(3)
c, Å	11.082(2)	15.016(2)
α, β, γ, deg	69.74(2), 82.48(2), 73.14(2)	90, 111.48(1), 90
V, Å^3	775.3(2)	3262.3(9)
D_{calc}	1.860	1.876
Z	2	4
F(000)	428	1808
μ, cm^{-1}	19.2	18.3
cryst size, mm	0.35 × 0.17 × 0.13	0.18 × 0.14 × 0.10
	Data Collection	
temp, K	100	100
radiation	Mo Kα (Zr); 0.710 73 Å	Mo Kα (Zr); 0.710 73 Å
$\theta_{min}/\theta_{max}$, deg	1.96, 27.50	1.06, 27.5
scan type	$\omega/2\theta$	$\omega/2\theta$
Δω, deg	0.60 + 0.35 tan θ	0.88 + 0.35 tan θ
horiz and vert aperture, mm	3.0, 5.0	3.76, 5.0
ref rflns	310; 0,3,−1; 101	−2,6,0; 124; −4,0,2
data set	−11 to +11; −11 to +11; −14 to +14	−15 to +12; −25 to 0; −18 to +19
total no. of data	7533	8359
no. of unique data	3543 (R_{int} = 0.038)	7472
no. of obsd data	3207 ($I > 2.5\sigma(I)$)	4953 ($I > 2.5\sigma(I)$)
	Refinement	
N_{ref}, N_{par}	3207, 212	4953, 422
R, R_w, *S*	0.0224, 0.0289, 0.77	0.0377, 0.0360, 3.18
weighting scheme	$w^{-1} = \sigma^2(F) + 0.000243F^2$	$w^{-1} = \sigma^2(F) + 0.000613F^2$
av shift error	0.038	0.038
max/min residual density, e Å^{-3}	0.76, −0.51 (near Ru)	0.73, −0.90 (near Ru)

Complex 7. Data were collected for an orange block-shaped crystal mounted on top of a glass fiber. Unit cell parameters were determined from a least-squares treatment of the SET4 setting angles of 25 reflections with 12.5 < θ < 21.2°. The unit cell parameters were checked for the presence of higher lattice symmetry.[12] Data were corrected for Lp and for a small linear decay (2.5%) of the intensity control reflections during the 54 h of X-ray exposure time, but not for absorption. The H atoms of C(7) were located from a difference Fourier map and included in the refinement with free positional parameters. Other H atoms were introduced on calculated positions (C–H = 0.98 Å) and included in the refinement riding on their carrier atoms with one common isotropic thermal parameter (*U* = 0.028(2) Å^2). All non-hydrogen atoms were refined with anisotropic thermal parameters. Weights were introduced in the final refinement cycles; convergence was reached at *R* = 0.0224 and R_w = 0.0289 ($w^{-1} = \sigma^2(F) + 0.000243F^2$).

Complex 8I. Data were collected for a brown block-shaped crystal mounted on top of a glass fiber. Unit cell parameters were determined from a least-squares treatment of the SET4 setting angles of 25 reflections in the range 10.6 < θ < 19.2°. The unit cell parameters were checked for the presence of higher

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Table II. Final Coordinates and Equivalent Isotropic Thermal Parameters for the Non-Hydrogen Atoms of 7

atom	*x*	*y*	*z*	*U*(eq),[a] Å^2
Ru	0.22265(2)	0.43177(2)	0.22370(2)	0.0113(1)
Fe	0.10991(4)	0.73449(4)	0.23938(3)	0.0126(1)
O(1)	0.1465(2)	0.1700(2)	0.47252(17)	0.0231(5)
O(2)	0.3558(2)	0.2150(2)	0.05803(18)	0.0275(6)
O(3)	−0.1167(2)	0.4817(2)	0.13745(17)	0.0228(5)
O(4)	0.1780(2)	0.5435(2)	0.50938(16)	0.0215(5)
O(5)	−0.2459(2)	0.7835(2)	0.25286(18)	0.0241(5)
O(6)	0.0883(2)	1.0531(2)	0.25581(19)	0.0274(6)
N	0.4547(2)	0.4358(2)	0.27416(18)	0.0155(5)
C(1)	0.5877(3)	0.3030(3)	0.3476(2)	0.0198(7)
C(2)	0.6382(3)	0.1672(3)	0.2900(3)	0.0291(8)
C(3)	0.5404(3)	0.2433(3)	0.4896(2)	0.0248(7)
C(4)	0.4763(3)	0.5788(3)	0.2302(2)	0.0185(7)
C(5)	0.3522(3)	0.7075(3)	0.1519(2)	0.0180(6)
C(6)	0.2373(3)	0.6575(3)	0.1013(2)	0.0165(6)
C(7)	0.1095(3)	0.7842(3)	0.0341(2)	0.0196(7)
C(8)	0.1813(3)	0.2625(3)	0.3826(2)	0.0161(6)
C(9)	0.3137(3)	0.2930(3)	0.1225(2)	0.0190(6)
C(10)	0.0104(3)	0.4637(3)	0.1703(2)	0.0172(6)
C(11)	0.1554(3)	0.6114(3)	0.4022(2)	0.0163(6)
C(12)	−0.1063(3)	0.7600(3)	0.2505(2)	0.0166(6)
C(13)	0.0959(3)	0.9302(3)	0.2472(2)	0.0182(7)

[a] *U*(eq) = one-third of the trace of the orthogonalized **U** tensor.

lattice symmetry.[12] The crystal reflected rather poorly and showed relatively broad reflection profiles. Data were corrected for Lp and for a small linear decay (2.5%) of the intensity control reflections during the 124 h of X-ray exposure time, but not for absorption. H atoms were introduced on calculated positions (C–H = 1.02 Å) and included in the refinement riding on their carrier atoms with one common isotropic thermal parameter (U = 0.033(4) Å^2). All non-hydrogen atoms were refined with anisotropic thermal parameters. Weights were introduced in the final refinement cycles; convergence was reached at $R = 0.0377$ and $R_w = 0.0360$ ($w^{-1} = \sigma^2(F) + 0.000261F^2$).

Results

First, the formation reactions of the new heteronuclear complexes will be discussed; details about the characterization of these compounds will follow afterward.

Formation of 2 and 3. The thermal reaction of HFeRu(CO)$_5${RC=C(H)C(H)=N-iPr} (1) did not yield the anticipated Fe$_2$Ru$_2$-chain analogues of Ru$_4$(CO)$_{10}${RC=C(H)C(H)=NR′}$_2$ (12) by dimerization of two molecules of 1 and loss of H$_2$ (Figure 2). After 16-h reflux of **1b** in heptane primarily decomposition was observed. In the case of **1a** a new complex was obtained as the main product (37%), which appeared to be the dinuclear complex FeRu(CO)$_6${PhCC(H)C(H)N=C(Me)$_2$} (**2**) (Figure 3).

From the spectroscopic data it could be inferred (*vide infra*) that **2** contains a dehydrogenated iPr group; therefore, C–H activation must have occurred in the course of the reaction. A moderate quantity (12%) of another new complex, **3**, was isolated as well and separated from the former compounds by column chromatography. This dark red complex appeared to be FeRu$_3$(CO)$_{10}${PhC=C(H)C(H)=N-iPr}$_2$ (**3**) as indicated by FD-mass and elemental analysis. Complex **3** was selectively formed as a pure constitutional isomer and as one diastereomer, as could be concluded from the spectroscopic data (*vide infra*). Finally, negligible amounts of FeRu(CO)$_6${PhCC(H)C(H)N(H)-iPr} (**9**; both diastereomers **9aI** and **9aII** in a 1:1 ratio) were observed.

Formation of 4, 5, and 7. As thermal dimerization of 1 to Fe$_2$Ru$_2$(CO)$_{10}${RC=C(H)C(H)=N-iPr}$_2$ appeared not to be very successful, we examined the same reaction in the presence of a potential hydrogen-accepting substrate, i.e. an alkene. This approach has been applied before in the homonuclear case, but only for Ru$_2$(CO)$_6${MeC=C(H)CH$_2$N-iPr} (**10b**) in reaction with the activated alkenes isopropylcrotonaldimine and crotonaldehyde, which resulted in the selective formation of **13** (Figure 2).[2] In the heteronuclear case first **1a** was treated at 90 °C with styrene. This reaction appeared to provide a clean route to complex **2** with reasonable yields (61%); complex **3** was absent from the reaction mixture now.

When **1a** was heated with tBuCH=CH$_2$, complex **4** (Figure 4) was isolated as the main product, the structure of which has been elucidated from the spectroscopic data

Table III. Final Coordinates and Equivalent Isotropic Thermal Parameters for the Non-Hydrogen Atoms of 8I

atom	*x*	*y*	*z*	*U*(eq),[a] Å^2
Ru(1)	1.09918(4)	0.16191(2)	0.18835(3)	0.0139(1)
Ru(2)	0.87255(4)	0.14243(2)	0.20898(3)	0.0123(1)
Ru(3)	1.27698(4)	0.22655(2)	0.15465(3)	0.0172(1)
Fe(1)	0.77051(7)	0.05302(4)	0.27853(5)	0.0148(2)
O(1)	0.9128(3)	0.2834(2)	0.2985(3)	0.0223(12)
O(2)	0.7695(4)	0.2137(2)	0.0132(3)	0.0261(12)
O(3)	0.6326(3)	0.1821(2)	0.2214(3)	0.0207(12)
O(4)	0.7392(4)	0.0663(2)	0.4610(3)	0.0283(14)
O(5)	0.5492(4)	−0.0255(2)	0.2165(3)	0.0299(16)
O(6)	0.9859(4)	0.1548(2)	−0.0271(3)	0.0281(14)
O(7)	1.1037(4)	0.0069(2)	0.2008(3)	0.0254(12)
O(8)	1.1812(4)	0.2802(3)	−0.0545(3)	0.0388(17)
O(9)	1.4062(4)	0.1225(2)	0.0780(3)	0.0344(16)
O(10)	1.4884(4)	0.3200(2)	0.2558(3)	0.0355(17)
N(1)	0.8283(4)	0.0363(2)	0.1670(3)	0.0163(12)
N(2)	1.1577(4)	0.2723(2)	0.2110(3)	0.0170(12)
C(1)	0.7532(5)	0.0069(3)	0.0715(4)	0.1096(17)
C(2)	0.6444(5)	0.0502(3)	0.0191(4)	0.0275(19)
C(3)	0.8310(6)	−0.0027(4)	0.0123(5)	0.033(2)
C(4)	0.8788(5)	−0.0127(3)	0.2364(4)	0.0199(17)
C(5)	0.9438(5)	0.0134(3)	0.3257(4)	0.0166(17)
C(6)	0.9551(5)	0.0864(3)	0.3337(4)	0.0161(17)
C(7)	1.0247(5)	0.1147(3)	0.4301(4)	0.0149(17)
C(8)	1.1354(5)	0.0879(3)	0.4825(4)	0.0192(17)
C(9)	1.2014(5)	0.1143(3)	0.5732(4)	0.0257(17)
C(10)	1.1562(5)	0.1674(3)	0.6106(4)	0.0250(17)
C(11)	1.0473(6)	0.1954(3)	0.5590(4)	0.0265(19)
C(12)	0.9805(5)	0.1694(3)	0.4690(4)	0.0200(17)
C(13)	0.9034(5)	0.2288(3)	0.2636(4)	0.0182(17)
C(14)	0.8070(5)	0.1866(3)	0.0860(4)	0.0196(17)
C(15)	0.7101(5)	0.1439(3)	0.2296(4)	0.0191(17)
C(16)	0.7526(5)	0.0622(3)	0.3893(4)	0.0208(17)
C(17)	0.6365(5)	0.0056(3)	0.2370(4)	0.0202(17)
C(18)	1.0927(5)	0.3393(3)	0.1845(5)	0.0256(17)
C(19)	1.1829(6)	0.3974(3)	0.2164(6)	0.039(2)
C(20)	1.0165(6)	0.3445(3)	0.0803(5)	0.037(2)
C(21)	1.1684(5)	0.2467(3)	0.2994(4)	0.0189(17)
C(22)	1.2411(5)	0.1890(3)	0.3312(4)	0.0189(17)
C(23)	1.2973(5)	0.1641(3)	0.2693(4)	0.0218(17)
C(24)	1.3797(5)	0.1032(3)	0.3032(5)	0.0282(19)
C(25)	1.0283(5)	0.1568(3)	0.0551(4)	0.0202(17)
C(26)	1.0965(5)	0.0662(3)	0.1962(4)	0.0197(17)
C(27)	1.2135(5)	0.2653(3)	0.0242(5)	0.0251(19)
C(28)	1.3589(5)	0.1616(3)	0.1070(4)	0.0239(17)
C(29)	1.4101(6)	0.2858(3)	0.2146(5)	0.026(2)

[a] *U*(eq) = one-third of the trace of the orthogonalized **U** tensor.

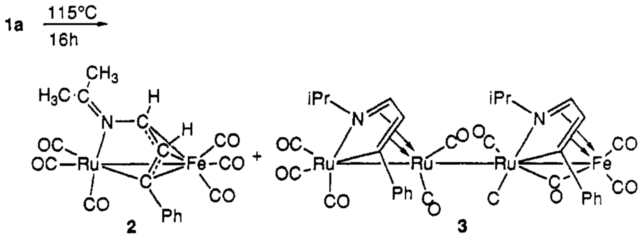

Figure 3. Thermal reaction of **1a**, affording complexes **2** and **3**.

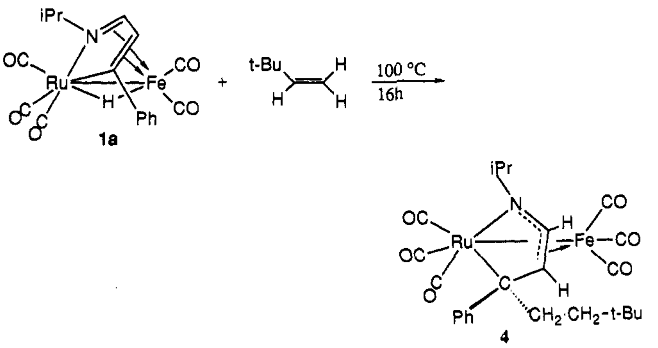

Figure 4. Reaction of **1a** with 3,3-dimethyl-1-butene, affording complex **4**.

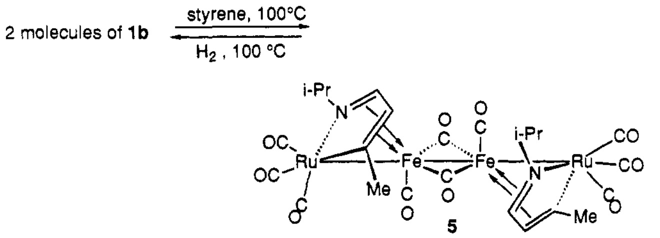

Figure 5. Interconversion between **1b** and the heteronuclear chain complex **5**.

(*vide infra*). It appeared that C–C coupling between the hydrogenated alkene and the monoazadienyl ligand had occurred. A small amount of a byproduct remained unidentified.

The reactivity of **1b** toward alkenes was found to differ completely from that of **1a**. When **1b** was heated with styrene at 100 °C over 0.5 h, **1b** was converted into $Fe_2Ru_2(CO)_{10}\{CH_3C{=}C(H)C(H){=}N\text{-}iPr\}_2$ (**5**) in high yield (Figure 5). Complex **5**, which according to the spectroscopic data is the desired heteronuclear analogue of **12**, appeared to be susceptible to hydrogenolysis, affording **1b** again.

Therefore, in the reaction of **1b** with styrene no dehydrogenation of the ligand system was observed, although especially in the case of R = Me in the homonuclear Ru_2 complexes dehydrogenation of the R group occurred.[13] The synthesis of **7** via another route showed that the anticipated heteronuclear analogue of **13**, *i.e.* complex **7**, actually can exist. As reported before,[1] the *in situ* prepared cationic complex $FeRu(CO)_6\{RC{=}C(H)C(H){=}N\text{-}iPr\}^+BF_4^-$ (**6**) appeared to be a useful starting complex for the synthesis of new heterodinuclear complexes (Figure 6). Upon chromatographing **6b** on silica, we succeeded in the isolation of **7** in moderate yields.

The same conversion could be brought about when **6b** was treated with H_2O, implying that the role of the silica is similar to the role of H_2O, i.e. abstraction of H^+. The molecular structure of **7** was verified by X-ray crystallography (*vide infra*). Complex **7** could be reconverted into **1b** by a reaction with H_2.

Formation of 8. Not only were alkenes used as hydrogen accepting substrates but also the unsaturated Ru_2 complex **13** was tested as starting complex for the synthesis of $FeRu_3$-chain complexes. Clean reaction between **1a** and **13** took place at 50 °C in heptane over 30 h, and a red solution was formed (Figure 7).

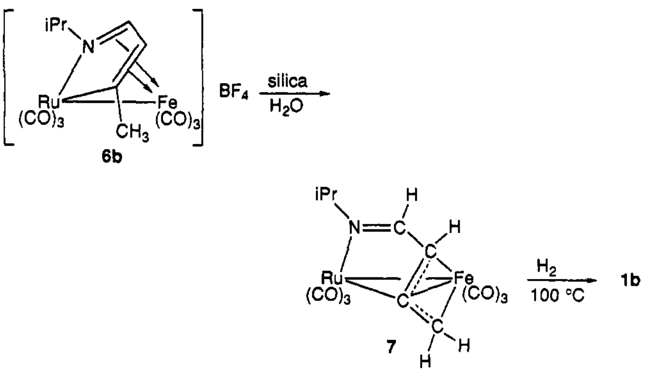

Figure 6. Formation reaction of **7** and its conversion with H_2 into **1b**.

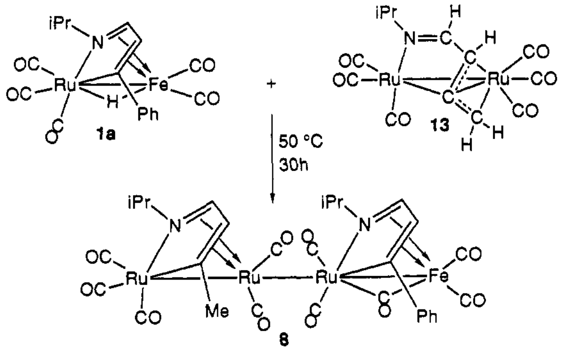

Figure 7. Formation of the mixed-ligand FeRu complex **8** from **1a** and **13**.

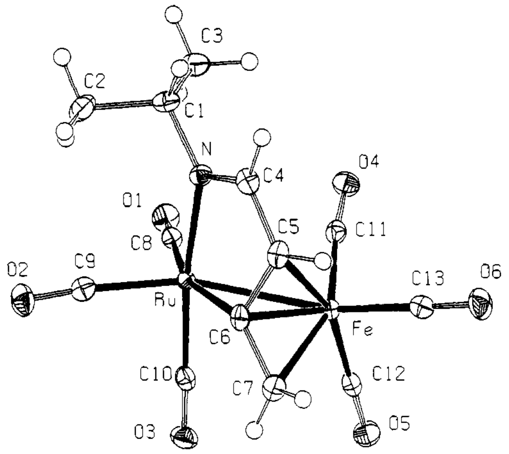

Figure 8. X-ray molecular structure of $FeRu(CO)_6\{C(H)_2CC(H)C(H){=}N\text{-}iPr\}$ (**7**).

The new heteronuclear chain cluster $FeRu_3(CO)_{10}(MeC{=}CHCH{=}N\text{-}iPr)(PhC{=}CHCH{=}N\text{-}iPr)$ (**8**) was formed in high yield and exists in equal amounts of both diastereomers. Complex **8** provides an example of a mixed-ligand complex, as two differently substituted monoazadienyl ligands are present. The structure of one diastereomer (**8I**) was analyzed by X-ray crystallography. It does not possess the Ru–Fe–Ru–Ru skeleton, which was expected by analogy with the formation of **12** (Figure 2), but instead a Ru–Ru–Ru–Fe frame appeared to be present.

Formation of $FeRu(CO)_6\{PhCC(H)C(H)N(H)\text{-}iPr\}$ (9aII). Because of the observed reactivity of **1a,b** with unsaturated substrates, we tested the performance of **1a,b** as a homogeneous catalyst in the catalytic hydrogenation of alkenes. In contrast to **1b**, complex **1a** readily catalyzed the hydrogenation of styrene at 50 °C (16 h, 1 mol % catalyst). With the sterically more hindered α-methyl-

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[13] Reaction of $Ru_2(CO)_6\{RC{=}C(H)CH_2N\text{-}iPr\}$ (**10**) with a 10-fold molar excess of styrene or 3,3-dimethyl-1-butene (DMB) at 100 °C for 16 h gave according to ^1H NMR the following results: (i) for styrene/**10a** 80% of **12a**; (ii) for styrene/**10b** 60% of **12b** and 40% of **13**; (iii) for DMB/**10b** 40% of **12b** and 60% of **13**.

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) for 7 (with Esd's in Parentheses)

Ru–Fe	2.7120(8)	Ru–N	2.1402(19)	Ru–C(6)	2.065(3)
Ru–C(8)	1.969(2)	Ru–C(9)	1.913(3)	Ru–C(10)	1.891(3)
Fe–C(5)	2.150(3)	Fe–C(6)	1.971(2)	Fe–C(7)	2.159(2)
Fe–C(11)	1.789(2)	Fe–C(12)	1.786(3)	Fe–C(13)	1.788(3)
O(1)–C(8)	1.130(3)	O(2)–C(9)	1.134(3)	O(3)–C(10)	1.138(3)
O(4)–C(11)	1.146(3)	O(5)–C(12)	1.147(3)	O(6)–C(13)	1.141(3)
N–C(1)	1.481(3)	N–C(4)	1.284(3)	C(1)–C(2)	1.516(4)
C(1)–C(3)	1.517(3)	C(4)–C(5)	1.442(4)	C(5)–C(6)	1.435(4)
C(6)–C(7)	1.406(4)				
N–Ru–C(6)	79.97(9)	C(5)–Fe–C(6)	40.47(10)	C(5)–Fe–C(7)	67.48(10)
C(6)–Fe–C(7)	39.47(10)	Ru–N–C(1)	130.41(15)	Ru–N–C(4)	111.66(16)
C(1)–N–C(4)	117.9(2)	N–C(4)–C(5)	118.5(2)	Fe–C(5)–C(4)	114.61(16)
Fe–C(5)–C(6)	63.05(14)	C(4)–C(5)–C(6)	115.7(2)	Ru–C(6)–Fe	84.39(9)
Ru–C(6)–C(5)	107.98(16)	Ru–C(6)–C(7)	127.4(2)	Fe–C(6)–C(5)	76.48(14)
Fe–C(6)–C(7)	77.50(15)	C(5)–C(6)–C(7)	114.8(2)	Fe–C(7)–C(6)	63.03(12)

Table V. Selected Bond Distances (Å) and Bond Angles (deg) for 8I (with Esd's in Parentheses)

Ru(1)–Ru(2)	2.8902(9)	Ru(1)–Ru(3)	2.6890(8)	Ru(1)–N(2)	2.233(4)
Ru(1)–C(21)	2.267(6)	Ru(1)–C(22)	2.263(6)	Ru(1)–C(23)	2.255(6)
Ru(1)–C(25)	1.869(6)	Ru(1)–C(26)	1.853(6)	Ru(2)–Fe(1)	2.5569(10)
Ru(2)–N(1)	2.154(4)	Ru(2)–C(6)	2.075(6)	Ru(2)–C(13)	1.836(6)
Ru(2)–C(14)	1.922(6)	Ru(2)–C(15)	2.097(6)	Ru(3)–N(2)	2.114(5)
Ru(3)–C(23)	2.042(6)	Ru(3)–C(27)	1.917(7)	Ru(3)–C(28)	1.893(6)
Ru(3)–C(29)	1.910(7)	Fe(1)–N(1)	2.064(5)	Fe(1)–C(4)	2.081(6)
Fe(1)–C(5)	2.143(6)	Fe(1)–C(6)	2.174(6)	Fe(1)–C(15)	1.939(6)
Fe(1)–C(16)	1.763(6)	Fe(1)–C(17)	1.764(6)	O(1)–C(13)	1.164(7)
O(2)–C(14)	1.145(7)	O(3)–C(15)	1.163(7)	O(4)–C(16)	1.149(7)
O(5)–C(17)	1.154(8)	N(1)–C(1)	1.500(7)	N(1)–C(4)	1.375(7)
N(2)–C(18)	1.490(7)	N(2)–C(21)	1.377(7)	C(4)–C(5)	1.390(8)
C(5)–C(6)	1.415(8)	C(6)–C(7)	1.487(8)	C(21)–C(22)	1.391(8)
C(22)–C(23)	1.421(9)	C(23)–C(24)	1.504(9)		
Ru(2)–Ru(1)–Ru(3)	159.1(2)	Ru(1)–Ru(2)–Fe(1)	138.52(3)	C(1)–N(1)–C(4)	114.2(4)
C(18)–N(2)–C(21)	115.0(5)	N(1)–C(4)–C(5)	115.2(5)	C94)–C(5)–C(6)	116.0(5)
C(5)–C(6)–C(7)	116.3(5)	Ru(2)–C(13)–O(1)	173.9(6)	Ru(2)–C(14)–O(2)	178.8(6)
Ru(2)–C(15)–Fe(1)	78.5(2)	Ru(2)–C(15)–O(3)	139.0(5)	Fe(1)–C(15)–O(3)	142.3(5)
Fe(1)–C(16)–O(4)	177.9(5)	Fe(1)–C(17)–O(5)	175.1(5)	N(2)–C(21)–C(22)	116.3(5)
C(21)–C(22)–C(23)	116.1(5)	C(22)–C(23)–C(24)	117.3(5)	Ru(1)–C(25)–O(6)	178.6(5)
Ru(1)–C(26)–O(7)	174.6(6)	Ru(3)–C(27)–O(8)	171.5(6)	Ru(3)–C(28)–O(9)	179.0(6)
Ru(3)–C(29)–O(10)	175.5(6)				

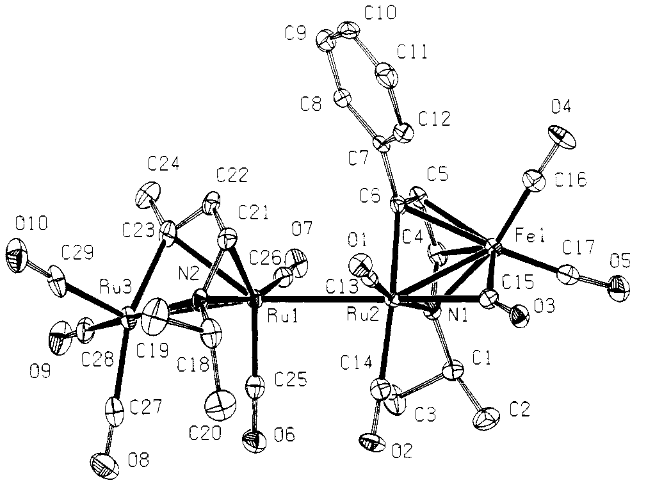

Figure 9. X-ray molecular structure of $FeRu_3(CO)_{10}\{PhC{=}C(H)C(H){=}N\text{-}iPr\}\{MeC{=}C(H)C(H){=}N\text{-}iPr\}$ (8I).

styrene only 20% conversion was observed under the same conditions. With aliphatic substituted alkenes such as 3,3-dimethyl-1-butene and maleic anhydride no reaction was observed at all. As the remaining organometallic species after the hydrogenation of styrene/α-methylstyrene, complex **9aII** was isolated, which is not active as a catalyst itself. The catalytic hydrogenation reaction reported here was not further optimized.

Molecular Structure of Complex 7. The molecular geometry of 7 is shown in Figure 8, and selected bond distances and angles are given in Table IV.

The $Ru(CO)_3$ and $Fe(CO)_3$ fragments in **7** are linked by a normal single Fe–Ru bond of 2.7120(8) Å, as compared to other FeRu carbonyl complexes with a formally single Fe–Ru bond, *e.g.* $FeRu(CO)_6$(iPr-DAB) (2.6602(9) Å).[14] The structure of **7** is further closely comparable to that of **13**.[4] The η^3-allyl coordination is characterized by the Fe–C(5) (2.150(3) Å), Fe–C(6) (1.971(2) Å), and Fe–C(7) (2.159(2) Å) distances. As in all allyl-type complexes, the metal–(central carbon) bond is shortened.[15] As compared to the corresponding distances in **13**, the bonds between Fe and the allyl C atoms in **7** are on average 0.10 Å shorter, which is expected when one takes into account the smaller covalent radius of Fe.

Molecular Structure of Complex 8I. The molecular geometry of **8I** is shown in Figure 9, and selected bond distances and angles are given in Table V.

The X-ray crystal structure of **8I** provides a definite answer with respect to the molecular geometry and stereochemistry of complex **8**. As expected, **8** is a heterotetranuclear chain complex, but surprisingly the Fe atom is not one of the middle atoms of the chain but a terminal one. The length of the outer Ru–Ru bond (Ru(1)–Ru(3) = 2.6890(8) Å) is comparable to the corresponding distance in the homonuclear complex **12** (2.7084 Å).[16] The central intermetallic bond of the Ru–Ru–Ru–Fe skeleton (Ru(1)–Ru(2) = 2.8920(9) Å) is rather long for

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[14] Zoet, R.; van Koten, G.; Muller, F.; Vrieze, K.; van Wijnkoop, M.; Goubitz, K.; van Halen, C. J. G.; Stam, C. H. *Inorg. Chim. Acta* **1988**, *149*, 193.

[15] Clarke, H. L. *J. Organomet. Chem.* **1974**, *80*, 369.

Table VI. IR Data for Compounds 2–9 (a, R = Ph; b, R = Me)[a]

	ν(CO), cm^{-1}						ν(N-H)/(μ-CO)
2	2074 (s)	2020 (vs)	2009 (s)	1985 (s)	1966 (s)	1952 (m)	
3	2072 (s)	2028 (vs)	2010 (s)	1995 (s)	1978 (m)	1970 (vs)	
					1949 (w)	1940 (w)	1862 (w)
4	2078 (m)	2047 (w)	2020 (vs)	2000 (m)	1989 (s)	1965 (s)	
5	2078 (m, sh)	2068 (vs)	2009 (s)	1995 (vs)	1958 (w)	1919 (w)	1768 (m, br)
7	2076 (s)	2025 (vs)	2009 (vs)	1995 (vs)	1972 (s)	1955 (m)	
8I	2069 (s)	2024 (vs)	2008 (s)	1990 (s)	1975 (m)	1967 (m)	
					1945 (w)	1937 (w)	1858 (w, br)
8II	2069 (s)	2024 (vs)	2007 (s)	1989 (s)	1978 (m)	1967 (m)	
					1950 (w)	1936 (w)	1860 (w, br)
9aII	2073 (s)	2020 (vs)	2009 (s)	1984 (s)	1968 (s)	1945 (m)	3190 (w)[b]

[a] In units of cm^{-1}. Conditions and definitions: hexane solution; $FeRu(CO)_6[RCC(H)C(H)N{=}C(CH_3)_2]$ (**2**), $FeRu_3(CO)_{10}[PhC{=}C(H)C(H){=}N\text{-}iPr]_2$ (**3**), $FeRu(CO)_6[PhC(CH_2CH_2\text{-}tBu)C(H)C(H)N\text{-}iPr]$ (**4**), $Fe_2Ru_2(CO)_{10}[MeC{=}C(H)C(H){=}N\text{-}iPr]_2$ (**5**), $FeRu(CO)_6[CH_2CC(H)C(H){=}N\text{-}iPr]$ (**7**), $FeRu_3(CO)_{10}[(PhC{=}C(H)C(H){=}N\text{-}iPr)(MeC{=}C(H)C(H){=}N\text{-}iPr)]$ (**8**), $FeRu(CO)_6[RCC(H)C(H)N(H)\text{-}iPr]$ (**9**). [b] Could only be detected when measured as a KBr pellet.

a single Ru–Ru bond. The Fe–Ru interaction (2.5569(10) Å), on the other hand, is significantly shortened as compared to the Fe–Ru bonds in $FeRu(CO)_6\{PhC(H)C(H)C(H)N\text{-}iPr\}$ (2.610(3) Å), $HFeRu(CO)_6\{PhC{=}C(H)C(H){=}N\text{-}iPr\}$ (2.7714(18) Å),[1] or **7** (2.7120(8) Å), which may be due to the presence of the bridging carbonyl ligand C(15)–O(3). Such a shortening effect has for example also been observed in $FeMn(CO)_6\{tBu\text{-}NC(H)C(H)N(H)\text{-}tBu\}$.[17] The Fe–C(15) (1.939(6) Å) and Ru(2)–C(15) bonds (2.097(6) Å) are both elongated by on average 0.15 Å compared to the M–C bonds of terminal CO ligands, which points to a rather symmetrical bridging mode. Also, the Ru(2)–C(15)–O(3) (139.0(5)°) and Fe–C(15)–O(3) (142.3(5)°) angles, which deviate to almost the same extent from 180°, are in support of this conclusion. The ligand part of the molecule features bonding properties that are quite comparable to other π-coordinated Ru-monoazadienyl etallacycles as in **12** (Figure 2). The most remarkable aspect is the bonding of the Ru(3)-containing metallacycle, in which the ligand part is coordinated with almost equal bond distances (2.250 ± 0.017 Å) to Ru(1). The chain-shaped metal framework deviates considerably from linearity, as is expressed in the intermetallic angles Ru(3)–Ru(1)–Ru(2) (159.12(2)°) and Ru(1)–Ru(2)–Fe(1) (138.52(3)°).

The structure of **8** exhibits some strikingly similar features as compared to the homonuclear chain complex $Ru_4(CO)_{10}\{C(H)_2C{=}C(H)C(H){=}N\text{-}tBu\}_2$, which is formed by thermal dimerization and C–C coupling of two molecules of **13**.[18]

First, the Ru atoms in the metallacycles form the central part of the molecule, as in the FeRu fragment in **8**. This is in contrast to the geometry of complex **12**, where both outer Ru atoms are cyclometalated (see Figure 2). Second, the central metal–metal bond in $Ru_4(CO)_{10}\{C(H)_2C{=}C(H)C(H){=}N\text{-}tBu\}_2$ is very long (2.8833(5) Å) and comparable to that in **8** (2.8920(8) Å). The outer Ru–Ru bonds are bridged by a carbonyl ligand, as for the FeRu fragment in **8**. The feature of a bridging carbonyl ligand is directly related to the inversion of the geometry of the cyclometalated Ru atom from the outside of the chain to the inside; the resulting electronic situation is complemented by one bridging carbonyl ligand. Finally, the chain molecule $Ru_4(CO)_{10}\{C(H)_2C{=}C(H)C(H){=}N\text{-}tBu\}_2$ with intermetallic angles of about 138° deviates significantly from linearity, as is also the case in **8**. This is probably caused by the hybridization at Ru(2), which formally has seven ligands in its coordination sphere.

By analogy to the tetraruthenium complexes **12**,[19] the chirality of the Ru(2) and Ru(3) centers in complex **8I** can be described both as *OC*-6-33-*A*.[19,20] As the crystal of **8I** contains the enantiomers (*CC*)-**8I** and (*AA*)-**8I**, complex **8II** consists of the *CA*/*AC* diastereomeric pair.

Spectroscopic Analysis. Spectroscopic data for the new heteronuclear complexes **2**–**9** are given in Tables VI–VIII.

Tetranuclear Complex 5. The NMR spectra of **5** show four sets of resonances, indicating that **5** is present as four isomers. As the differences in chemical shift between each isomer are small, the molecular geometries of these isomers are likely to resemble each other. Most characteristic features for the establishment of the geometry in **5** are the absorption band at 1768 cm^{-1} in the IR spectrum and the resonances around 270 ppm in the ^{13}C spectrum, which point to the presence of bridging carbonyl ligands. The H_{im}/C_{im} and H_α/C_α resonances at about 6.1/124.0 and 4.6/105.0 ppm, respectively, are indicative for a MAD-yl ligand in the 7e coordination mode.[1,19] These data are completely in line with the data found for the homonuclear complex **12**, which possesses the structure, as depicted in Figure 2. Due to the presence of chiral Ru atoms and the possibility of a mutual *cis* or *trans* arrangement of the two azaruthenacycles, complex **12** may exist as four physically distinct isomers, as visualized schematically in Figure 10.

In the NMR spectra of **12** only two isomers were observed at room temperature, which was shown to be due to a rapid (on the NMR time scale) *cis*/*trans* isomerization reaction between *trans*-(*AC*/*CA*)-**12** and *cis*-(*AC*/*CA*)-**12** and between *trans*-(*AA*/*CC*)-**12** and *cis*-(*AA*/*CC*)-**12** (Figure 10). These dynamic processes could be frozen out at 183 K, showing the expected four sets of signals.[21]

Interestingly, the NMR spectra of **5** at room temperature strongly resemble the low-temperature (183 K) NMR spectra of the homonuclear analogue **12**. Hence, no *cis*/

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(16) Polm, L. H.; Mul, W. P.; Elsevier, C. J.; Vrieze, K.; Christophersen, M. J. N.; Stam, C. H. *Organometallics* **1988**, *7*, 423.

(17) Keijsper, J.; Mul, J.; van Koten, G.; Vrieze, K.; Ubbels, H.; Stam, C. H. *Organometallics* **1984**, *3*, 1732.

(18) Mul, W. P.; Elsevier, C. J.; van Leijen, M.; Vrieze, K.; Spek, A. L. *Organometallics* **1991**, *10*, 533.

(19) Elsevier, C. J.; Mul, W. P.; Vrieze, K. *Inorg. Chim. Acta* **1992**, *198–200*, 689. It should be noted that the Fe atom and Ru(1) are chiral as well, but since their chirality is related to the chirality of Ru(2) and Ru(3), this does not provide additional information and has therefore been omitted.

(20) Nomenclature according to: IUPAC. *Nomenclature of Inorganic Chemistry, Recommendations 1990*; Blackwell: Oxford, England, 1990; p 171.

(21) Mul, W. P.; Ernsting, J.-M.; de Lange, W. G. J.; van Straalen, M. D. M.; Vrieze, K.; Elsevier, C. J.; de Wit, M.; Stam, C. H. *J. Am. Chem. Soc.*, in press.

Table VII. ^{1}H NMR Data[a] for Compounds 2–9 (a, R = Ph; b, R = Me)

	H_{im}	H_{α}	iPr	R	N–H/R′
2[c]	5.03 (d, 3.0)	5.68 (d, 3.0)	2.09 (s)	7.60–7.17 (m)	
3[c]	6.63 (d, 2.1)	4.83 (d, 2.2)	3.35 (sept, 6.4), 1.20/1.13 (d, 6.4)	7.37–6.75 (m)	
	6.80 (d, 2.1)	6.48 (d, 2.1)	2.57 (sept, 6.5), 1.14/1.07 (d, 6.5)		
4[c]	6.64 (d, 2.7)	3.94 (d, 2.7)	3.95 (sept, 6.4), 1.76/1.67 (d, 6.4)	7.40–7.03 (m)	2.43/1.30 (m) 0.92/0.70 (m), 0.76 (s)
5d1[d]	5.94 (s)	4.75 (s)	3.37 (sept, 6.2), 1.20/1.05 (d, 6.2)	2.69 (s)	
5d2	6.51 (s)	4.56 (s)	3.64 (sept, 6.3), 1.30–0.81 (m)	2.40 (s)	
5e1	6.09 (s)	4.65 (s)	3.55 (sept, 6.3), 1.30–0.81 (m)	2.60 (s)	
5e2	6.16 (s)	4.62 (s)	3.68 (sept, 6.3),1.30–0.81 (m)	2.51 (s)	
7[b]	8.08 (d, 1.9)	3.03 (d, 2.0)	3.64 (sept, 6.5), 1.26/1.20 (d, 6.5)	3.37 (s, anti), 4.05 (s, syn)	
8I[c]	6.57 (br d)	4.51 (d, 2.0)	3.25 (sept, 6.5), 1.12/1.08 (d, 6.5)	7.28–6.95 (m)	
	6.86 (d, 2.1)	6.60 (d, 2.1)	2.57 (sept, 6.5), 1.13/1.08 (d, 6.5)		2.43 (s)
8II	7.28 (d, 1.8)	5.28 (d, 1.8)	3.11 (sept, 6.5), 1.16/1.00 (d, 6.4)	7.28–7.00 (m)	
	6.92 (d, 2.0)	6.59 (d, 2.0)	2.69 (sept, 6.5), 1.11/1.06 (d, 6.4)		2.41 (s)
9aII[c]	4.23 (d, 3.3)	5.54 (d, 3.3)	3.14 (dsept, 10.8, 6.3), 1.27/1.21 (6.3)	7.56–7.25 (m)	2.02 (br d, 10.8)

[a] In units of ppm (*J* values in Hz). Definitions: **d1**, *trans*-(*AC*/*AC*) isomer; **d2**, *trans*-(*AA*/*CC*) isomer; ratio **d1**/**d2** ≈ 1.2/1; **e1**, *cis*-(*AA*/*CC*) isomer; **e2**, *cis*-(*AC*/*CA*) isomer; ratio **e1**/**e2** ≈ 1.5/1. [b] 100 MHz, $CDCl_3$, 293 K. [c] 300 MHz, $CDCl_3$, 293 K. [d] 300 MHz, $CDCl_3$, 223 K.

Table VIII. ^{13}C NMR Data[a] for Compounds 2–9 (a, R = Ph; b, R = Me)

	C_{im}	C_{α}	C_{β}	C_{iPr}	R	CO_{Fe}	CO_{Ru}
2[c]	70.9	89.5	167.6	167.0, 30.9/20.8	148.8, 129.0, 128.1, 127.0	213.7	198.2, 198.0, 191.7
3[c]	135.3	105.5	182.0	63.3, 28.6/27.9	150.3, 128.2/126.2	240.6, 210.9, 209.7	207.4, 206.8, 203.2
	117.6	93.1	179.9	61.0, 26.5/25.2	148.8		198.7, 194.2, 192.0
4[b]	104.4	76.2	29.9	64.3, 29.5/24.2	151.2, 127.4, 123.4, 51.2, 38.2 ($-CH_2-$) 49.4, 29.1 (tBu)	213.2	197.9, 192.9, 187.0
5d1[e,i]	122.5	105.4	189.2	61.6, 27.2/27.0	33.2	270.7, 214.7	198.7, 194.0, 192.1
5d2	122.4	104.6	188.2	61.7, 27.1/26.9	32.8	274.1, 267.1, 214.8	198.6, 194.0, 192.1
5e1[f]	126.7	104.5	192.4	60.3, not obsd	33.3	271.4, 215.8	198.9, 194.2, 192.6
5e2	124.9	105.9	not obsd	60.2, not obsd	33.4	277.8, 266.0, 215.7	192.7, not obsd
7[d]	178.7	70.5	194.6[g]	62.7, 24.3/23.9	63.7	214.6 (217.7, 214.6, 211.5)[h]	199.4, 197.7, 190.8
8I[c]	136.6	105.8	181.2	63.8, 29.4/28.3	151.2, 128.7, 127.4, 126.9	242.1, 211.8, 210.6	208.4, 207.6, 204.4
	117.7	95.6	181.0	61.8, 27.1/26.0	34.0		204.2, 200.4, 194.8, 192.5
8II	136.7	106.3	182.1	63.5, 28.7/28.0	150.7, 128.2, 127.7, 126.8	240.7, 211.9, 210.8	206.6, 205.0, 204.2
	116.7	97.8	181.2	63.1, 27.8/25.8	33.7		203.6, 200.5, 194.4, 192.3
9aII	65.4	86.7	170.3	55.3, 25.3/22.2	149.2, 129.7, 128.8, 127.9	214.8	199.3, 198.6, 192.0

[a] In units of ppm (*J* values in Hz). [b] 75.46 MHz, $CDCl_3$, 263 K. [c] 75.46 MHz, $CDCl_3$, 293 K. [d] 25.1 MHz, $CDCl_3$, 263 K. [e] Definitions: **d1**, *trans*-(*AC*/*CA*) isomer; **d2**, *trans*-(*AA*/*CC*) isomer; ratio **d1**/**d2** ≈ 1.2/1. [f] Definitions: **e1**, *cis*-(*AA*/*CC*) isomer; **e2**, *cis*-(*AC*/*CA*) isomer; ratio **e1**/**e2** ≈ 1.5/1. [g] Assigned by means of intensity considerations when compared to the ^{13}CO resonances. [h] 62.9 MHz, $CDCl_3$, 233 K. [i] 75.46 MHz, $CDCl_3$, 223 K.

trans isomerization occurs in **5** at 293 K. Attempts to observe *cis*/*trans* isomerization at higher temperatures failed, because when the temperature was raised the NMR sample started to decompose slowly.

From the four isomers present in the spectra of **5** two isomers are predominantly present, corresponding to the spectra **d1** and **d2** (in amounts of about 45% and 40%, respectively) in Tables VII and VIII. These spectra should be assigned to the *trans* isomer of each diastereomer, i.e. *trans*-(*AC*/*CA*)-**5** and *trans*-(*AA*/*CC*)-**5**, because on steric grounds they will be the thermodynamically more stable isomers. Especially the bridging carbonyl region of the ^{13}C NMR spectrum provides the information which is necessary for further structural assignment. Because spectrum **d1** (Table VIII) features only one bridging carbonyl resonance at 270.7 ppm, it is assigned to the *trans*-(*AC*/*CA*) isomer of **5**, which features two isochronous bridging CO's. In *trans*-(*AA*/*CC*)-**5**, however, both bridging CO's are anisochronic and give rise to two signals at 274.1 and 267.1 ppm (spectrum **d2**). The assignment of the spectra **e1** and **e2**, belonging to the *cis* isomers, can be effected by using the same arguments. Therefore, spectrum **e1** belongs to *cis*-(*AA*/*CC*)-**5** (10% yield) and the **e2** spectrum with the two bridging CO signals belongs to *cis*-(*AC*/*CA*)-**5**. The two diastereomers *AA*/*CC* and *AC*/*CA*, each divided into unequal amounts of noninterconverting *cis* and *trans* isomers, are present in approximately equal amounts.

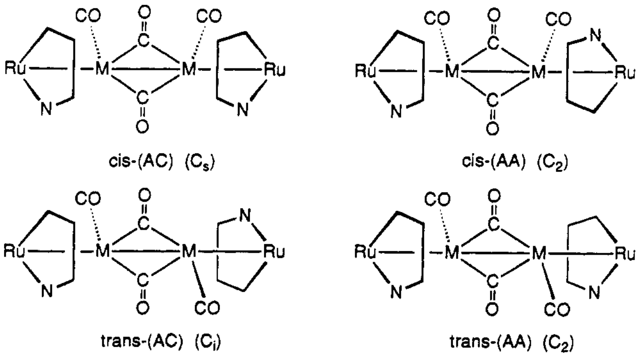

Figure 10. Carbonyl-bridged conformations of $Ru_2M_2(CO)_{10}\{MeC{=}C(H)C(H){=}N\text{-}iPr\}_2$ (**5**, M = Fe; **12**, M = Ru). The molecular symmetry is given in parentheses.

When the spectra of **5** are compared with those of **12**, the eye-catching difference is that the *cis*/*trans* isomerization process in the case of **5** has been completely stopped. Moreover, the CO scrambling process between bridging and terminal CO's, which takes place in **12** at 293 K and could not be stopped for the *trans*-(*AA*/*CC*) isomer even at 183 K,[21] does not occur in **5** at 293 K either. In the isolobal analogues of **5** and **12**, *i.e.* $[Fe(CO)_2Cp]_2$ and $[Ru(CO)_2Cp]_2$, respectively, a similar trend is observed. The activation energy for isomerization in $[Fe(CO)_2Cp]_2$ is higher than for $[Ru(CO)_2Cp]_2$,[22] and also in the Ru dimer with an highly substituted Cp ligand such as $C(Me)_4(Et)$ the isomerization was hampered.[22] The trends in the Cp complexes were explained on steric grounds, and probably the same steric effects will be responsible for the absence of fluxionality in the case of 5 in comparison with 12.

Tetranuclear Complexes 3 and 8. The NMR spectra of the complexes 8I and 8II strongly deviate from spectra for, *e.g.*, complex 12, the latter featuring two cyclometalated Ru atoms at the outside of the chain and two π-complexed Ru atoms at the inside. The NMR data for 8 implied a molecular geometry which differs from that of 12, which was the incentive to undertake the X-ray structure determination for 8I (*vide supra*). Some characteristic NMR and IR data are as follows. The resonances of H_{im} and H_α in the homonuclear complex are found at 7.48 and 6.88 ppm, respectively, which are values at extremely high frequency for a π,π-coordinated monoazadienyl ligand. On the basis of these data and by irradiation experiments, the pair H_{im}/H_α of the coupled resonances at 6.57/4.51 ppm has been assigned to the Ru_2 fragment in diastereomer 8I and the pair at 6.86/6.60 ppm to the FeRu unit. The corresponding ^{13}C resonances for C_{im}/C_α at 136.6/95.6 ppm have been assigned to the Ru_2 moiety and those at 117.7/105.8 ppm to the FeRu unit.

From the thermal reaction of **1a** also a tetranuclear complex of formula $FeRu_3(CO)_{10}\{PhC{=}C(H)C(H){=}N\text{-}iPr\}_2$ (3) was isolated. As the NMR data for 3 are completely similar to those for 8, we assign to complex 3 the same molecular geometry as was found for 8. In contrast to the formation of 8, complex 3 is formed and isolated as one diastereomer selectively.

Dinuclear Complexes 2 and 7. In the first part of this work,[1] complexes have been categorized on the basis of their specific ligand system. The complexes 2 and 7 form together a distinct category, because they both contain a dehydrogenated monoazadienyl ligand, either at the R substituent (R = Me, 7) or at the iPr group (2).

The IR spectra of 2 and 7 in comparison with each other and with those of the previously reported $FeRu(CO)_6$ complexes,[1] exhibit only minor differences. By means of NMR spectroscopy, however, these complexes can be easily distinguished. The coordination behavior of the ligand systems in both 2 and 7 has been encountered before in their homonuclear analogues, and the NMR data exhibit a great similarity. The influence of Fe in the NMR spectra of 7 is most clearly expressed by the resonances of the allyl part, which is directly bonded to Fe. H_α and H_{syn} underwent an upfield shift of 0.37 and 0.23 ppm, respectively. The homonuclear Ru_2 analogue of **2a** with the same R group is not known (only with R = Me),[23] and therefore a detailed comparison is not warranted. In general, however, the NMR data resemble each other very well, which allows the definite confirmation of the molecular geometry of 2.

Dinuclear Complex 4. Complex 4 (Figure 4), which is obtained from the reaction of **1a** with $tBuCH{=}CH_2$, shows spectroscopic features similar to those for $FeRu(CO)_6\{PhC(H)C(H)C(H)N\text{-}iPr\}$,[1] and therefore the same ligand coordination mode may be assumed. Most characteristic are the values for H_{im}/C_{im} (6.64 and 104.4 ppm) and H_α/C_α (3.94 and 76.2 ppm), which correlate very well with the corresponding data for $FeRu(CO)_6\{PhC(H)C(H)C(H)N\text{-}iPr\}$ (6.91/110.1 and 3.95/71.8 ppm, respectively). In contrast to the case for $FeRu(CO)_6\{PhC(H)C(H)C(H)N\text{-}iPr\}$, H_α in complex 4 is observed as a doublet, due to coupling with H_{im} only. Therefore, besides the R group (R = Ph), C_β carries another non-hydrogen group. By means of correlation spectroscopy (^1H–^1H and ^1H–^{13}C) four multiplets in the ^1H NMR spectrum could be assigned to a neopentyl substituent on C_β. The NMR spectra of 4 show only one set of signals, which implies that complex 4 is formed diastereoselectively (see Discussion).

Dinuclear Complexes 9aI and 9aII. Complex **9a** can exist as two diastereomers, due to the presence of the chiral Ru and N centers,[19] and both forms appeared to be selectively formed via two different syntheses. Complex **9aII** was obtained by serendipity from the catalytic hydrogenation experiment of styrene with complex **1a** as catalyst precursor. The other diastereomer, **9aI**, has been reported before[1] as a product of the reaction of **6a** (Figure 6) with $NaBH_4$. The NMR spectra of both diastereomers exhibit characteristic features and are assigned to the molecular structures depicted in Scheme III (*vide infra*). As could be expected, the greatest influence of the two different configurations at N is observed in the chemical shifts and coupling constants of the iPr group and the N–H group. The considerable low-frequency shift of the N–H resonance in **9aII** as compared to **9aI** (0.58 ppm), which is probably due to shielding effects by the proximity of the Ru atom, is in favor of assigning structure **II** to complex **9aII**. The iPr group then points away from the metal, and the methine proton resonating at 3.14 ppm likewise experiences little shielding influence of the metal. In structure **I** (Scheme III), assigned to **9aI**, the reverse holds. Finally, the difference of 100 cm^{-1} in IR frequency of the N–H vibrations for the two diastereomers points to a large diastereomeric distinction.

Discussion

Dimerization of 1. Compound **1b** needs an additive (*viz.* styrene) to effect its thermal dimerization, resulting in $Fe_2Ru_2(CO)_{10}\{MeC{=}C(H)C(H){=}N\text{-}iPr\}_2$ (**5**). Also, the thermal reaction in the case of **1a** has not provided a direct route to a tetranuclear Fe_2Ru_2 complex, but instead the dinuclear Fe–Ru complex 2 and the tetranuclear $FeRu_3$ complex 3 were formed. By use of styrene as an additive in this reaction, only the formation of 3 was inhibited, thus providing a selective route to 2. On the basis of the observed product formation in the thermal reaction of 1 and the effect of styrene on this reaction we propose the mechanism shown in Scheme I.[24]

By analogy with the mechanism of dimerization of $HFe(CO)_2Cp$[25] the first step in the thermal reaction of 1 probably is the loss of a H atom and formation of the radical intermediates **A** and **A′**. Dimerization of two molecules of **A**, featuring an Fe-centered radical, would lead to the expected Fe_2Ru_2 complex (**AA**) with a central Fe–Fe bond, as in the case of **1b**. In the case of **1a**, however, the dimer **AA** is not formed, which may have a steric reason, caused by the two rather bulky ruthenazadienyl rings. Because of the shorter covalent radius of Fe

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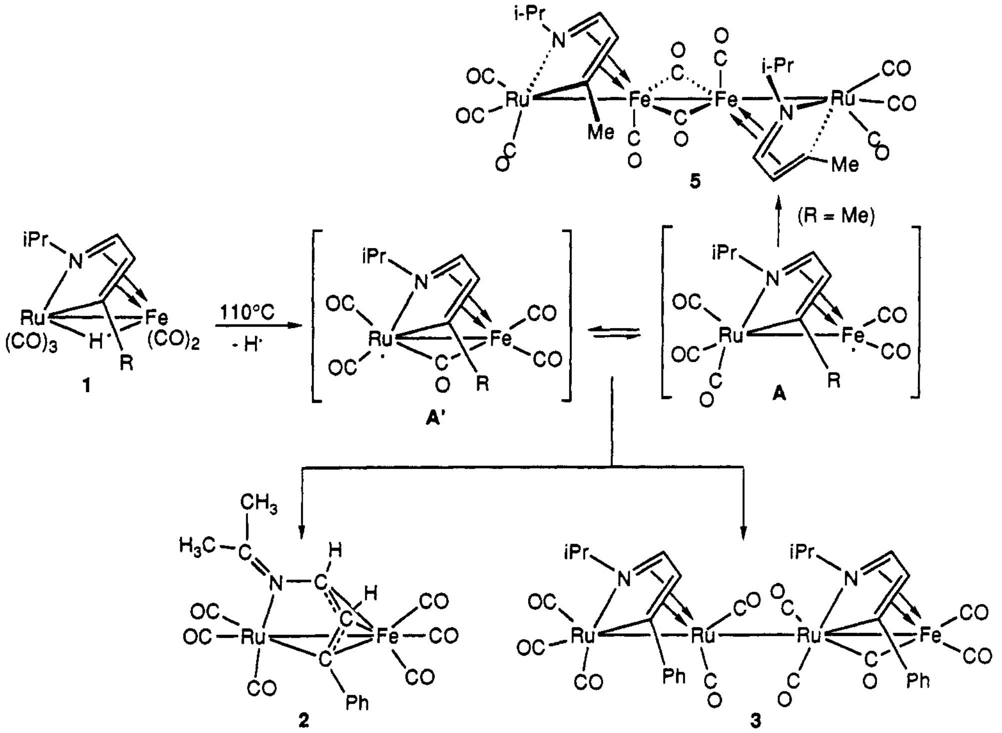
[22] (a) Gansow, O. A.; Burke, A. R.; Vernon, W. D. *J. Am. Chem. Soc.* **1972**, *94*, 2550. (b) Gansow, O. A.; Burke, A. R.; Vernon, W. D. *J. Am. Chem. Soc.* **1976**, *98*, 5817.

[23] Mul, W. P.; Elsevier, C. J.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1992**, *11*, 1891.

[24] A more detailed, speculative scheme can be obtained from the authors.

[25] (a) Shackelton, T. A.; Mackie, S. C.; Fergusson, S. B.; Johnston, L. J.; Baird, M. C. *Organometallics* **1990**, *9*, 2248. (b) Tyler, D. R.; Schmidt, M. A.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 6018. (c) Castellani, M. P.; Tyler, D. R. *Organometallics* **1989**, *8*, 2113.

Scheme I. Proposed Mechanism for the Thermal Reaction of Complex 1a



compared to Ru, the intermetallic distances in the dimer **AA** will be shorter than in the Ru_4 complex **12**, thus bringing the ruthenaazadienyl rings in closer contact. For the rather bulky Ph substituents in **1a** this effect can be expected to be larger than for the Me-substituted **1b**, which appeared to dimerize readily to **5** in the presence of styrene. Another reason for the observed R-group dependence of the reaction may be the extra stability of the intermediate **A′** in the case of R = Ph due to delocalization of the radical in the metallacycle and the conjugated Ph group. In this way the equilibrium between **A** and **A′** may be shifted to the side of **A′**, thus making dimerization of two molecules of **A** less likely.

The formation of **2** and **3** from the stage of intermediates **A** and **A′** can be explained by analogy to the formation of **2**, as reported earlier,[23] by activation of the methine C–H bond of the iPr group. Compound **3** is formed as a byproduct via complex intermolecular H-transfer and decomposition reactions.[24]

As can be inferred from Scheme I, the conversion of 5 equiv of **1a** is required for the production of 2 equiv of **2** and 1 equiv of **3**. The observed yield of **2** (37%) is close to the theoretical maximum yield of 40%, whereas the yield of **3** (12%) is a bit lower than the expected 20%.

Concerning the stereochemistry of the reaction, **3** can in principle be formed as a mixture of two diastereomers, but only one diastereomer has been observed. Due to the rather rigorous reaction conditions, the equilibrium between both diastereomers will be shifted to the side of the thermodynamically most stable diastereomer. This equilibrium requires breaking of the central intermetallic bond, which is quite reasonable under the reaction conditions employed.[21]

Reaction of Complex 1a with Complex 13: Formation of the Mixed-Ligand $FeRu_3$ Complex 8. In order to provide a better understanding of the factors which determine the stability of the heteronuclear chain complexes, we investigated the reaction of **1a** with **13**. The structure of the product **8**, featuring the unexpected Fe–Ru–Ru–Ru skeleton (*vide supra*), implies that during the formation of **8** the reactive spot of the $FeRu(CO)_5$ moiety must have shifted from Fe toward Ru. This process can be envisaged by the equilibrium between radical intermediates **A** and **A′**, depicted in Scheme I. Intermediate **A** may be formed after transfer of its hydride to complex **13**, thereby transforming **13** into $^{\bullet}Ru_2(CO)_6\{MeC{=}C(H)\text{-}C(H){=}N\text{-}iPr\}$ and subsequently upon loss of CO into $^{\bullet}Ru_2(CO)_5\{MeC{=}C(H)C(H){=}N\text{-}iPr\}$ (abbreviated as **X**). Apparently, combination of the **A′** and **X** particles to give **A′X** type tetranuclear species takes place selectively, as no **XX** or **AX** species are formed (**AA** is also not formed from **1a**, only from **1b** (*vide supra*), but **XX** is known to be a stable product).[16] Possibly, steric requirements are too large to form the **AX** combination. Alternatively, the selective formation of **8** may be ascribed to the formation of the more stable Ru–Ru bond (by combining **A′** with **X**) in that case as compared to an Fe–Ru bond (when combining **A** with **X**).[26]

C–C Coupling in the Reaction of 1a with 3,3-Dimethyl-1-butene. The reaction of **1a** with styrene appeared to provide a clean route to complex **2**. When 3,3-dimethyl-1-butene was used, the reaction took an entirely different course and the formation of the new dinuclear product **4** was observed, which contains a ligand system in which the alkene has been incorporated. This finding can best be explained by assuming a process as depicted in Scheme II.

Under thermal conditions the alkene can compete with the π(C=N) coordination of the monoazadienyl ligand to Fe. Subsequently, insertion of the alkene into the Fe–H bond may occur with concomitant recoordination of the π(C=N) interaction to Fe. The last step in the formation of the main reaction product **4** is the transfer of the alkyl group, bonded at Fe, toward the C_β atom of the monoaza-

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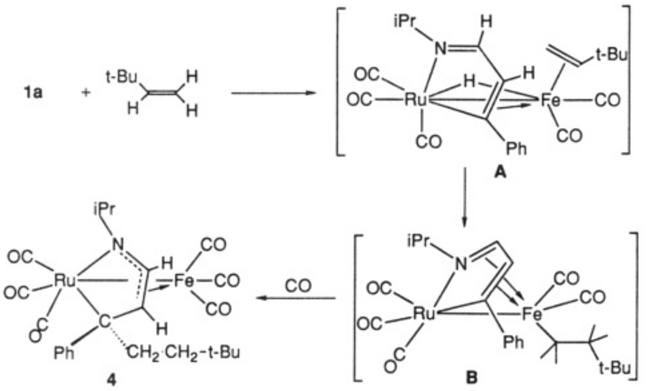
[26] Yawney, B. W.; Stone, F. G. A. *J. Chem. Soc. A* **1969**, 502.

Scheme II. Proposed Mechanism for the Formation of 4

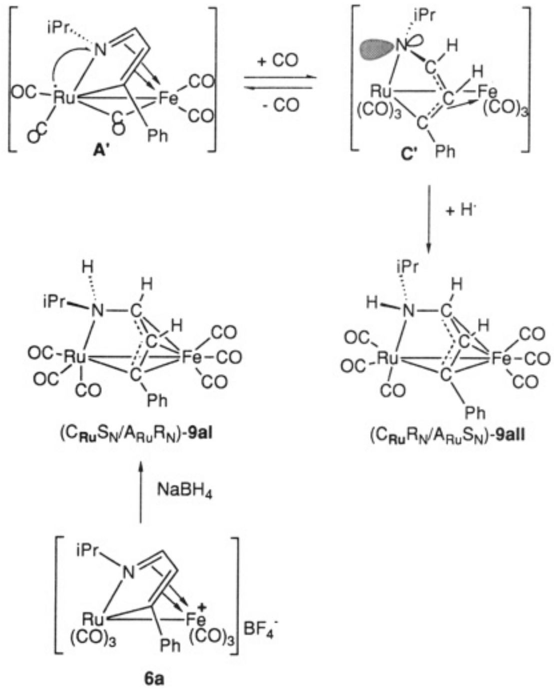


dienyl ligand and the uptake of an additional CO ligand. The transfer of the alkyl group takes place analogously to the hydride transfer in **1a**, yielding FeRu(CO)$_6${PhC(H)C(H)C(H)N-iPr},[1] which analogy is apparent both from the regioselective transfer of the hydride/alkyl group to C_β and from the complete diastereoselectivity of the formation of both complexes. Moreover, the alkene insertion takes place with complete regioselectivity at the alkene (see Scheme II, **B**).

The difference in reactivity between styrene and 3,3-dimethyl-1-butene can be explained by invoking the relative stability of the Fe–alkyl bond in intermediate **B**, which will be more stable for the insertion product from 3,3-dimethyl-1-butene as compared to the case of styrene, resulting in the remarkable formation of **4**. Such an alkyl transfer reaction finds precedent in the chemistry of (C_5Me_5)Fe(CO)$_2$CH$_2$Ph (an isolobal analogue of intermediate **B**), which could be converted photochemically into (η^4-$C_5Me_5(CH_2Ph)$)Fe(CO)$_3$ via a radical mechanism.[27]

Catalytic Hydrogenation of Alkenes. As styrene influences the thermal reactions of **1a,b**, it seemed logical to investigate the catalytic hydrogenation reaction of styrene, using **1a,b** as a homogeneous catalyst. In fact, styrene can be catalytically hydrogenated at 50 °C, at 1.2 bar of H_2, using 1 mol % of complex **1a** (with **1b** no hydrogenation could be effected under these conditions). The workup of the reaction products, however, did not afford complex **1a**, but instead the new complex **9aII** (see Scheme III) could be isolated. Therefore, during the catalytic reaction one of the diastereomers of **9a** was formed selectively. Complex **9aII** was not active as a catalyst itself under the same conditions, which was confirmed by a separate experiment. Additional information about the reaction mechanism was obtained by performing the reaction with D_2 instead of H_2. The intention was to let the reaction run for a short time (about 2 h), so that a few catalytic cycles should have been passed through. Workup of the reaction mixture did not afford the expected complex DFeRu(CO)$_5$[PhC=C(H)C(H)=N-iPr}, but instead a small amount of unreacted and unlabeled **1a** was recovered together with a large amount of decomposed material. This implies that **1a** is a precursor of the actual catalyst, which is too unstable to be isolated. In order to gain more insight into the nature of the catalytic process, three other alkenes were tested under the same conditions as well. In the case of α-methylstyrene only 20% was hydrogenated to cumene. Performance of this reaction under D_2 instead of H_2 gave **9aII** with complete incorporation of the D label on N.

Scheme III. Formation of 9aI and 9aII



The presence of **9aII** after the reaction is probably due to a lapse of the catalytic cycle. Small amounts of CO will be formed from decomposed catalyst molecules, which then can react with intermediates such as **A** and **A′** (Scheme I), as these intermediates can be expected to have a reasonable lifetime. Apparently, **A′** reacts selectively with CO via **C′** (see Scheme III) to give **9aII**.

An important aspect concerns the origin of the hydrogen atom which is present on the N atom in **9aII**, which may originate from the added H_2, from intermediates, or from the solvent. As the reaction of **1a** with styrene or α-methylstyrene under D_2 has revealed that the N–D-labeled complex **9aII** was obtained exclusively, the solvent (*i.e.* totally or partially hydrogenated alkene molecules) can be excluded as the hydrogen source, because in the case of styrene at least 50% of the N–H product should be expected, instead of the observed 100% of N–D-labeled complex.

Interestingly, compound **9aI**, which has been obtained by reduction of the cationic intermediate complex **6a** with NaBH$_4$,[1] represents the other pure diastereomer. The stereoselectivity of the process by which **9aI** and **9aII** are formed is intriguing, but the precise mechanism for the formation of these compounds remains as yet unclear.[24]

Influence of Heteronuclearity on the Conversion of 7 with H₂. Complex **1b** can be re-formed from **7** (Figures 6 and 8) by reaction with H_2 at 100 °C. After 3 h, 40% of **7** appeared to be converted into **1b**. A similar conversion has been reported for the homonuclear analogue **13** (100 °C, 0.5 h, 75% yield of **10b**) and was believed to involve an η^3–η^1 flip of the allyl moiety, thus providing an open coordination site for oxidative addition of H_2.[28]

When the hydrogenation of **7** is compared with the similar reaction of the homonuclear system (**13** with H_2), two interesting points come up. First, from the much shorter reaction time of **13** it might be concluded that the homonuclear system is much more reactive. When **7**

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[27] Paw Blaha, J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 2694.

[28] Mul, W. P.; Elsevier, C. J.; van Leijen, M.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1992**, *11*, 1877.

follows the same mechanism as **13**, this means that now oxidative addition of H_2 must take place on a 16-electron Fe center instead of a Ru center. Because one of the prerequisites for the reaction of a transition metal (d^8) complex with H_2 is the high basicity of the metal,[29] and because Ru is more basic than Fe, the Ru system exhibits a greater reactivity than the FeRu system. The second remarkable feature is that under the same reaction conditions the ligand system in the Ru_2 case ends up in a double-reduced state, whereas the ligand on the FeRu framework ends in the single-reduced form. This may be related to the reactivity of an intermediate in both systems, i.e. $HMRu(CO)_6\{RC{=}C(H)C(H){=}N\text{-}iPr\}$ (M = Fe, Ru). Under thermal conditions in the absence of CO, a CO ligand in the FeRu complex is substituted by the π(C═N) bond of the monoazadienyl ligand.[1] In the Ru_2 case, however, the hydride is transferred, yielding **10**.[28] Probably, this difference in reactivity is caused by the much stronger π coordination to Fe as compared to Ru, making the hydride transfer reaction less favorable in the case of the FeRu complex case as compared to the Ru_2 complex.

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Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom parameters, and bond distances and bond angles for **7** and **8I** (9 pages). Ordering information is given on any current masthead page.

OM920703S

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(29) Brothers, P. J. *Prog. Inorg. Chem.* **1981**, *28*, 1.