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Preparation and properties of FeRu(CO)$_5$(L)(α-diimine) (α-diimine = R-DAB, R-Pyca; L = PR$_3$, CO); the reduction of the coordinated 1,4-diaza-1,3-butadiene to dianionic 1,2-diaminoethane by reaction with hydrogen

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Abstract

FeRu(CO)$_6$(^{i}Pr-Pyca) (**1a**) reacts with hydrogen to give the highly reactive species H$_2$FeRu(CO)$_5$(^{i}Pr-Pyca) (**2**), which contains a bridging and a terminal hydride atom. Treatment of **2** with CX$_4$ affords HFeRu(X)(CO)$_5$(^{i}Pr-Pyca) (X = Cl (**3a**); I (**3b**)) in which the terminal hydride has been substituted. Complex **2** reacts back with carbon monoxide to give FeRu(CO)$_6$(^{i}Pr-Pyca) (**1a**), whereas treatment of **2** with PMe$_2$Ph gives FeRu(CO)$_5$(PMe$_2$Ph)(^{i}Pr-Pyca) (**4b**). Complexes **4** can easily be prepared from the hexacarbonyl complexes FeRu(CO)$_6$(α-diimine) (α-diimine = ^{i}Pr-Pyca (**1a**); ^{i}PR-DAB (**1b**)) and the appropriate phosphine, giving FeRu(CO)$_5$(PR$_3$)(α-diimine) (α-diimine = ^{i}Pr-Pyca, PR$_3$ = PPh$_3$ (**4a**); α-diimine = ^{i}Pr-Pyca, PR$_3$ = PMe$_2$Ph (**4b**); α-diimine = ^{i}Pr-DAB, PR$_3$ = PPh$_3$ (**4c**); α-diimine = ^{i}Pr-DAB, PR$_3$ = PMe$_2$Ph (**4d**)) in high yields. Reaction of FeRu(CO)$_5$(PPh$_3$)(^{i}Pr-DAB) (**4c**) with hydrogen at 90 °C yields FeRu(CO)$_5$(PPh$_3$)(^{i}Pr-N-CH$_2$CH$_2$-N-^{i}Pr) (**5**). The use of deuterium showed that the reduction proceeds stereoselectively, giving solely the *trans*-addition product FeRu(CO)$_5$(PPh$_3$)(^{i}Pr-N-C(H)(D)C(H)(D)-N-^{i}Pr) (**5′**). Complex **5** can easily be converted by carbon monoxide to FeRu(CO)$_6$(^{i}Pr-N-CH$_2$CH$_2$-N-^{i}Pr) (**8**). The conversion of **8** to **5** can be performed also, albeit less facile than the conversion of **5** to **8**. The hydrogenation of both **1b** and **4c** was inhibited by carbon monoxide and free triphenylphosphine. In the latter case the new complexes FeRu(CO)$_4$(PPh$_3$)$_2$(α-diimine) (α-diimine = ^{i}Pr-Pyca (**6a**); ^{i}Pr-DAB (**6b**)) were formed. A single crystal X-ray structure determination of **6a** was obtained. Red crystals of **6a** (C$_{49}$H$_{42}$N$_2$O$_4$P$_2$FeRu, $M_r = 941.8$, $Z = 2$) are triclinic, space group $P\bar{1}$ and have cell constants $a = 11.625(3)$, $b = 14.269(3)$, $c = 15.963(2)$ Å, $\alpha = 90.95(1)$, $\beta = 100.23(1)$ and $\gamma = 101.95(2)°$. A total of 5886 reflections was used in the refinement which converged to a final R value of $R = 0.064$. Reaction of MRu(CO)$_6$(^{i}Pr-DAB)(M = Fe (**1b**); Ru (**1c**)) with 40 bar of carbon monoxide at 90 °C afforded Ru(CO)$_3$(^{i}Pr-DAB) and M(CO)$_5$ (M = Fe, Ru). Interestingly it was found that reaction of Ru(CO)$_3$(DAB) with H$_2$Fe(CO)$_4$ also produced FeRu(CO)$_6$(^{i}Pr-N-CH$_2$CH$_2$-N-^{i}Pr) (**8**), whereas D$_2$Fe(CO)$_4$ afforded only the *trans* deuterated compound FeRu(CO)$_6$(^{i}Pr-N-C(H)(D)C(H)(D)-N-^{i}Pr) (**8′**). Finally attention has been focussed on the elucidation of the mechanism of this *trans* addition of H$_2$/D$_2$ to the central C–C bond of the coordinated 1,4-diaza-1,3-butadiene.

Introduction**

The hydrogenation of small molecules containing C–N multiple bonds in general is not a facile process. Solid state catalysts are usually employed and elevated temperatures and pressures are needed while the reactions proceed with low selectivity [1, 2]. The use of transition metal clusters as homogeneous catalysts is of great interest [3], since metal-atom clusters permit a greater variety of interactions with substrates than is possible in mononuclear complexes. Accordingly hydrogenation and dehydrogenation reactions of cluster bound C–N multiple bond systems have been well studied and examples are known for each step of the reaction sequence $\mathrm{C{\equiv}N \rightleftharpoons C{=}N \rightleftharpoons C{-}N}$ [1, 2, 4–6].

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**R-DAB = 1,4-diaza-1,3-butadiene; R-N=CHCH=N-R. R-Pyca = pyridine-2-carbaldimine; C$_5$H$_4$N-C(H)=N-R. In this paper only R = ^{i}Pr will be used.

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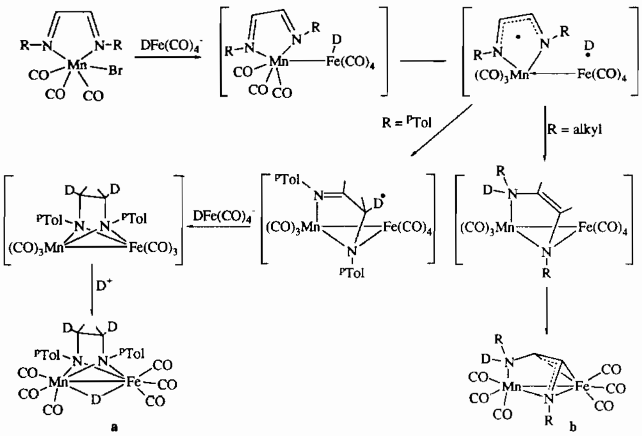
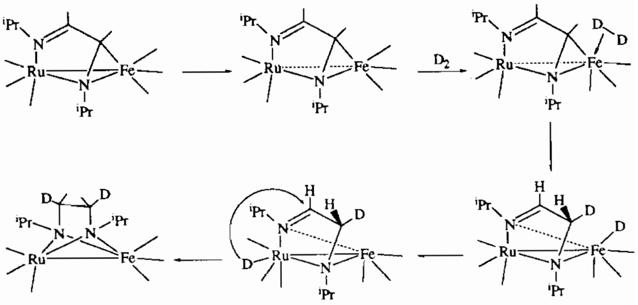
It is known that Mn(Br)(CO)$_3$(R-DAB) R = ^{p}Tol), containing a 4e donating σ-N, σ-N′ coordinated DAB ligand reacted with HFe(CO)$_4^-$ to produce FeMn(CO)$_6$(H)(^{p}Tol-N-CH$_2$CH$_2$-N-^{p}Tol) (Scheme 1, structure **a**) [7]. In this complex a formally dianionic diamido ligand is present, resulting from a transfer of the iron hydride atom(s) to the C atoms of the C=N moieties. Interestingly the use of DFe(CO)$_4^-$ resulted in a stereoselective *trans* addition of the D atoms to the two C atoms of the NCCN skeleton. This reaction, which might very well proceed via a single electron transfer mechanism, was only observed for R = ^{p}Tol. For R = alkyl the only product was FeMn(CO)$_6$[RNC(H)C(H)NHR], which contains an azaallylic moiety (Scheme 1, structure **b**). In the latter case the hydride has been transferred to the imine N atom of a C=N moiety [7, 8].



Scheme 1. Proposed mechanism for the formation of (μ-D)FeMn(CO)$_6$(^{p}Tol-N-C(H)(D)C(H)(D)-N-^{p}Tol) (**a**) and FeMn(CO)$_6$[RNC(H)C(H)N(D)(R)] (**b**) [7, 8].

Recently the reaction of FeRu(CO)$_6$(R-DAB) with hydrogen has been reported yielding a hydrogenated DAB ligand R-N-CH$_2$CH$_2$-N-R [6] (Scheme 2). The use of D$_2$ showed that the addition proceeds in a *trans* manner with respect to the NCCN skeleton. The favoured proposed mechanism for this reaction is shown in Scheme 2 and involves first a (partial) rupture of the Fe–Ru bond. The D$_2$ is now added at the Fe atom which, as shown by models, has more space available than the Ru atom. The selective *trans* addition has been explained by a transfer of the second deuteride ligand from the iron centre to the ruthenium centre during the hydrogenation process.

In order to elucidate this tentative mechanism in greater detail we extended this research by carrying out reactions of FeRu(CO)$_6$(^{i}Pr-Pyca) and of FeRu(CO)$_5$(PR$_3$)(^{i}Pr-DAB) with H$_2$/D$_2$, both with and without additional ligands.



Scheme 2. Proposed mechanism for the hydrogenation of FeRu(CO)$_6$(^{i}Pr-DAB) [6].

Experimental

Materials and apparatus

^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker AC-100, WM-250 and AMX-300 spectrometers. IR spectra (ν(CO); 2200–1600 cm^{-1}) were measured on a Perkin-Elmer 283 spectrometer. Elemental analyses were carried out by the section elemental analyses of the Institute of Applied Chemistry TNO, Zeist, Netherlands or by Dornis und Kolbe, Microanalytisches Laboratorium, Mülheim, Germany. All preparations were carried out under an atmosphere of purified nitrogen, using carefully dried solvents. Column chromatography was performed using silica gel (Kieselgel 60, Merck, 70-230 Mesh ASTM, dried and activated before use) as the stationary phase. Ru$_3$(CO)$_{12}$ (Strem) and PPh$_3$ (Merck) were used as commercially obtained. PMe$_2$Ph (Aldrich) was distilled prior to use. Me$_3$NO (Aldrich) was dried before use by heating *in vacuo*. CI$_4$ (Aldrich) was washed with hexane several times before use in order to remove I$_2$ impurities. Complexes FeRu(CO)$_6$(^{i}Pr-N-CH$_2$CH$_2$-N-^{i}Pr) [6], FeRu(CO)$_6$(^{i}Pr-Pyca) [9], FeRu(CO)$_6$(^{i}Pr-DAB) [10], Ru$_2$(CO)$_6$(^{i}Pr-DAB) [11, 12] and Ru$_2$(CO)$_5$(IAE) [11] were prepared according to literature procedures.

High pressure NMR experiments were performed using a home built apparatus consisting of a Ti/Al/V pressure head and a 10 mm external and 8.4 mm internal diameter sapphire NMR tube suitable for measurements up to 140 bar gas pressure [13]. A volume of 1.5 ml of a C$_6$D$_6$ solution was syringed into the sapphire tube which was kept under an atmosphere of dinitrogen using a special designed glass vessel. Subsequently the tube was connected to a high pressure system, and pressurized with the desired gas. The NMR tube was then closed, disconnected from the high pressure system and the reaction was monitored by means of NMR spectroscopy.

Preparation of $H_2FeRu(CO)_5(^iPr\text{-}Pyca)$ (2)[*]

(a) Thermally

A total of 300 mg of $FeRu(CO)_6(^iPr\text{-}Pyca)$ (**1a**) (0.63 mmol) was dissolved in 70 ml of heptane and stirred under an atmosphere of hydrogen at 85 °C[**]. The hydrogen atmosphere was refreshed regularly and the reaction was monitored by means of IR spectroscopy. The reaction was stopped when IR spectroscopy indicated the conversion was about half-way (about 100 h). The reaction mixture was purified by column chromatography. Elution with ligroin afforded a pale yellow fraction containing $H_2FeRu(CO)_5(^iPr\text{-}Pyca)$ (**2**) in about 20% yield. Elution with ligroin/CH_2Cl_2 (9/1) gave an orange fraction containing the unreacted **1a**.

(b) Using Me_3NO

A total of 300 mg of $FeRu(CO)_6(^iPr\text{-}Pyca)$ (**1a**) (0.63 mmol) was dissolved in 40 ml of benzene (or toluene) and a stream of hydrogen was slowly passed through the solution. After 15 min the addition of Me_3NO (120 mg of dry Me_3NO, dissolved in 4 ml of CH_2Cl_2) started in portions of 0.5 ml using intervals of 5 min, while hydrogen was still bubbled through the reaction mixture. The reaction was monitored by means of IR spectroscopy and the reaction was stopped when the conversion was virtually completed (usually 5 portions of Me_3NO were required, i.e. about 1.6 equiv.). The mixture could now be used for further reactions (*vide infra*) or evaporated to dryness and purified by column chromatography as described above. In this way complex **2** could be isolated in about 40% yield.

Synthesis of $HFeRu(X)(CO)_5(^iPr\text{-}Pyca)$ (3a, b)

A freshly prepared solution of **2** (see (b) above) was filtered over celite, evaporated to dryness and extracted with CH_2Cl_2 (30 ml). The solution was then treated with 1 ml CCl_4 (**3a**) or with 350 mg CI_4 (**3b**). IR spectroscopy indicated an instantaneous conversion of **2** to $HFeRu(X)(CO)_5(^iPr\text{-}Pyca)$ (X = Cl (**3a**); I (**3b**)). The reaction mixture was then evaporated to dryness and purified by column chromatography. Elution with ligroin/CH_2Cl_2 (9/1) in some cases afforded a small orange fraction containing traces of unreacted **1a**. The product $HFeRu(X)(CO)_5(^iPr\text{-}Pyca)$ (**3a**, **b**) was eluted with ligroin/CH_2Cl_2 (1/1) and evaporation of the solvent yielded **3a**, **b** in about 50% yield (based on **1a**).

Reaction of $H_2FeRu(CO)_5(^iPr\text{-}Pyca)$ (2) with PMe_2Ph to give $FeRu(CO)_5(PMe_2Ph)(^iPr\text{-}Pyca)$ (4b)

A solution of **2**, freshly prepared via the procedure of (b) above, was treated with 75 μl of PMe_2Ph. IR spectroscopy indicated an instantaneous and complete conversion to $FeRu(CO)_5(PMe_2Ph)(^iPr\text{-}Pyca)$ (**4b**). The reaction mixture was then evaporated to dryness and purified by column chromatography. Only one fraction was obtained upon elution with ligroin/CH_2Cl_2 (7/3) which after evaporation of the solvent yielded **4b** in about 50% yield (based on **1a**).

Reaction of $H_2FeRu(CO)_5(^iPr\text{-}Pyca)$ (2) with carbon monoxide to give 1a

A total of 300 mg of **1a** (0.63 mmol) was treated with hydrogen and Me_3NO as described above (see (b)). Once the conversion of **1a** to **2** was complete the stream of hydrogen was replaced by a stream of carbon monoxide and the reaction was monitored by means of IR spectroscopy. During the reaction the absorptions belonging to complex **2** gradually decreased and were replaced by those belonging to **1a**. After 50 min the reaction was completed and **1a** could be isolated in about 80% yield (based on the starting amount of **1a**) by evaporation of the solvent and subsequent extraction with hexane.

Synthesis of $FeRu(CO)_5(PR_3)(\alpha\text{-diimine})$ (α-diimine = ^iPr-Pyca, $PR_3 = PPh_3$ (4a); α-diimine = ^iPr-Pyca, $PR_3 = PMe_2Ph$ (4b); α-diimine = ^iPr-DAB, $PR_3 = PPh_3$ (4c); α-diimine = ^iPr-DAB, $PR_3 = PMe_2Ph$ (4d))

To 0.5 mmol of $FeRu(CO)_6(\alpha\text{-diimine})$ (α-diimine = ^iPr-Pyca (**1a**); ^iPr-DAB (**1b**)) in hexane 0.55 mmol of the appropriate phosphine was added. The product started precipitating within a few minutes while the reaction mixture was stirred for about 30 min. After this period IR spectroscopy indicated that the reaction was finished. The reaction mixture was filtered over celite, the residue was washed with hexane several times and extracted from the filter with CH_2Cl_2. Complexes **4a–d** could be isolated in more than 85% yield by evaporation of the solvent. Analytically pure samples were obtained by crystallization from hexane/CH_2Cl_2 at −20 °C. When CH_2Cl_2 or benzene were used as solvent the reaction time increased to several hours instead of about 30 min.

Synthesis of $FeRu(CO)_5(PPh_3)(^iPr\text{-}N\text{-}CH_2CH_2\text{-}N\text{-}^iPr)$ (5)

A total of 350 mg of $FeRu(CO)_5(PPh_3)(^iPr\text{-}DAB)$ (**4c**) (0.5 mmol) was dissolved in 50 ml of toluene and stirred under an atmosphere of hydrogen at 110 °C. The hydrogen atmosphere was refreshed regularly and the reaction was monitored by means of IR spectroscopy. When IR spectroscopy indicated the conversion was complete (about 10 h) the reaction mixture was evap-

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[*] Since preparation of a DAB complex analogous to **2** would be of interest for hydrogenation experiments we reacted $FeRu(CO)_6(^iPr\text{-}DAB)$ (**1b**) with Me_3NO in the presence of molecular hydrogen. Although IR spectroscopy indicated that traces of $H_2FeRu(CO)_5(^iPr\text{-}DAB)$ were possibly formed attempts to isolate this complex failed (see also ref. 10).

[**] It is important for the reaction temperature not to exceed 90 °C since then extensive decomposition of **2** is observed.

orated to dryness and subsequently purified by column chromatography. Upon elution with ligroin a pale yellow fraction was obtained which, after evaporation of the solvent, yielded FeRu(CO)$_6$(^{i}Pr-N-CH$_2$CH$_2$-N-^{i}Pr) (**8**) in 12–15% yield. Elution with ligroin/CH$_2$Cl$_2$ (8/2) afforded a yellow fraction which after evaporation of the solvent yielded FeRu(CO)$_5$(PPh$_3$)(^{i}Pr-N-CH$_2$CH$_2$-N-^{i}Pr) (**5**) in 60–65% yield.

Reversible interconversion between FeRu(CO)$_5$(PPh$_3$)(^{i}Pr-N-CH$_2$CH$_2$-N-^{i}Pr) (5) and FeRu(CO)$_6$(^{i}Pr-N-CH$_2$CH$_2$-N-^{i}Pr) (8)

Conversion of 8 to 5

FeRu(CO)$_6$(^{i}Pr-N-CH$_2$CH$_2$-N-^{i}Pr) (**8**) [6] (300 mg, 0.64 mmol) was dissolved in 50 ml of toluene and stirred at 110 °C in the presence of an excess of PPh$_3$ (0.8 g, 3.05 mmol) while the reaction was monitored by means of IR spectroscopy. After 70 h the mixture was evaporated to dryness and purified by column chromatography. Upon elution with ligroin a pale yellow fraction was isolated containing 80 mg of the starting complex FeRu(CO)$_6$(^{i}Pr-N-CH$_2$CH$_2$-N-^{i}Pr) (**8**). The reaction product FeRu(CO)$_5$(PPh$_3$)(^{i}Pr-N-CH$_2$CH$_2$-N-^{i}Pr) (**5**) was obtained by elution with ligroin/CH$_2$Cl$_2$ (8/2) as a yellow fraction and isolated in 70% yield (95% based on the amount of starting complex consumed).

Conversion of 5 to 8

A total of 200 mg of FeRu(CO)$_5$(PPh$_3$)(^{i}Pr-N-CH$_2$CH$_2$-N-^{i}Pr) (**5**) was dissolved in 30 ml of toluene and stirred under an atmosphere of carbon monoxide at 60 °C while the reaction was monitored by means of IR spectroscopy. After the conversion to FeRu(CO)$_6$(^{i}Pr-N-CH$_2$CH$_2$-N-^{i}Pr) (**8**) [6] was complete (about 30 min) the reaction mixture was evaporated to dryness. Both ^{1}H NMR and ^{31}P NMR of the residue dissolved in CDCl$_3$ indicated a complete conversion to FeRu(CO)$_6$(^{i}Pr-N-CH$_2$CH$_2$-N-^{i}Pr) (**8**) and free triphenylphosphine.

Reaction of FeRu(CO)$_6$(^{i}Pr-DAB) (1b) with hydrogen, with and without carbon monoxide

A total of 150 mg of FeRu(CO)$_6$(^{i}Pr-DAB) (**1b**) was dissolved in 40 ml of heptane and stirred at 95 °C. Hydrogen and carbon monoxide were bubbled through a reverse-flow bubbler with approximately equal velocity and led into a mixing chamber. The gas mixture was then bubbled through the heptane solution of **1b** while the reaction was monitored by means of IR spectroscopy. After 4 h IR spectroscopy indicated that no changes in the composition of the reaction mixture had occurred. Subsequently the introduction of carbon monoxide was stopped and only hydrogen was bubbled through the reaction mixture, resulting in a complete conversion of **1b** to FeRu(CO)$_6$(^{i}Pr-N-CH$_2$CH$_2$-N-^{i}Pr) (**8**) within 1.5 h.

Reaction of FeRu(CO)$_5$(PPh$_3$)(^{i}Pr-DAB) (4c) with hydrogen, with and without triphenylphosphine

A total of 1.0 g of FeRu(CO)$_5$(PPh$_3$)(^{i}Pr-DAB) (**4c**) was dissolved in 100 ml of toluene and stirred at 100 °C under an atmosphere of hydrogen. At the same time two comparable experiments were carried out in the presence of one and three equivalents triphenylphosphine (0.37 and 1.12 g, respectively). During the reactions samples of 10 ml were withdrawn from the reaction mixtures and analyzed by IR spectroscopy. The samples were separately evaporated to dryness and analyzed by ^{1}H NMR spectroscopy (250 MHz, C$_6$D$_6$ solution). The NMR data indicated a conversion of **4c** to **5** in the absence of triphenylphosphine. However, in the presence of triphenylphosphine no hydrogenation of the DAB ligand was observed, but instead **6b** was detected together with a substantial amount of decomposition. The complex **6b**, which is analogous to **6a**, could not be isolated in a pure form.

Synthesis of FeRu(CO)$_4$(PPh$_3$)$_2$(^{i}Pr-Pyca) (6a)

A mixture of 350 mg FeRu(CO)$_5$(PPh$_3$)(^{i}Pr-Pyca) (**4a**) (0.5 mmol) and 660 mg triphenylphosphine was refluxed in toluene (60 ml) while the reaction was monitored by means of IR spectroscopy. The reaction was stopped when IR spectroscopy indicated that the 1900 cm^{-1} absorption of Ru(CO)$_3$(PPh$_3$)$_2$ [14] became important. The reaction mixture was then evaporated to dryness, dissolved in 5 ml CH$_2$Cl$_2$ and purified by column chromatography. Elution with ligroin/CH$_2$Cl$_2$ (7/3) afforded an orange–red fraction containing the unreacted **4a** (about 50%). A red–brown fraction was obtained by elution with ligroin/CH$_2$Cl$_2$ (1/1) which, after evaporation of the solvent, yielded FeRu(CO)$_4$(PPh$_3$)$_2$(^{i}Pr-Pyca) (**6a**) in about 20% yield. Elution with ligroin/ CH$_2$Cl$_2$ (2/8) gave a pale yellow fraction containing Ru(CO)$_3$(PPh$_3$)$_2$ [14].

Reaction of Ru(CO)$_3$(^{i}Pr-DAB) with H$_2$Fe(CO)$_4$ and D$_2$Fe(CO)$_4$

An aqueous solution of Na$_2$Fe(CO)$_4$ was prepared starting from 24 g Ba(OH)$_2$·8H$_2$O, 10 g KOH and 11 ml Fe(CO)$_5$ in 60 ml water [15]. A solution of Ru(CO)$_3$(^{i}Pr-DAB) was prepared by treatment of Ru$_2$(CO)$_5$(IAE) (150 mg) in toluene (100 ml) with carbon monoxide at 90 °C for 30 min [16]. Subsequently the toluene solution of Ru(CO)$_3$(^{i}Pr-DAB) was frozen at a temperature of −196 °C. About 100 ml of an aqueous solution of H$_2$SO$_4$ (2.5 M) was added dropwise to the solution of Na$_2$Fe(CO)$_4$ over a period of 30 min. During this time a steady stream of carbon monoxide was allowed to sweep off the vapour of H$_2$Fe(CO)$_4$

through a drying tube of $CaCl_2$ and a trap cooled to 0 °C into the reaction vessel with the frozen toluene solution of $Ru(CO)_3(^iPr\text{-}DAB)$ [17]. The $H_2Fe(CO)_4$ was deposited upon the reaction mixture as a white solid. After the addition of the H_2SO_4 had finished the stream of carbon monoxide was continued for another 30 min in order to sweep off all the gaseous $H_2Fe(CO)_4$ into the reaction vessel with the frozen toluene solution of $Ru(CO)_3(^iPr\text{-}DAB)$. Subsequently the reaction mixture was slowly allowed to reach room temperature* and the reaction was monitored by means of IR spectroscopy once the toluene solution had become liquid. At a temperature of 0 °C the colour of the reaction mixture changed from red to dark purple. Since IR spectroscopy indicated there was still some $H_2Fe(CO)_4$ present, the mixture was stirred at 40 °C for 30 min and subsequently evaporated to dryness. Extraction with heptane afforded a dark green extract containing $Fe_3(CO)_{12}$ and $FeRu(CO)_6(^iPr\text{-}N\text{-}CH_2CH_2\text{-}N\text{-}^iPr)$ (**8**). Subsequent extraction of the residue with CH_2Cl_2 yielded a purple extract containing $Fe_2Ru(CO)_{10}(^iPr\text{-}DAB)$ (**7**) (10% yield) together with $Fe_3(CO)_{12}$. The green extract was concentrated to 60 ml and refluxed for 1.5 h to remove $Fe_3(CO)_{12}$**. Subsequent filtration and evaporation of the solvent yielded **8** in 30 % yield.

Use of $D_2Fe(CO)_4$, prepared from $DFe(CO)_4^-$ [8] and D_2SO_4 in D_2O, resulted in the formation of $FeRu(CO)_6(^iPr\text{-}N\text{-}C(H)(D)C(H)(D)\text{-}N\text{-}^iPr)$ (**8′**) as the major product. ^1H NMR spectroscopy indicated a *trans* addition of the two D atoms to the central C–C bond [6].

*Reaction of $M_2(CO)_6(^iPr\text{-}DAB)$ (M_2=FeRu (**1b**); Ru_2 (**1c**)) with carbon monoxide under high pressure*

A total of 50 mg of $M_2(CO)_6(^iPr\text{-}DAB)$ (M_2=FeRu (**1b**); Ru_2 (**1c**)) was dissolved in 1.5 ml of C_6D_6 and syringed into the HP-NMR tube (*vide supra*). The tube was pressurized with 40 bar of carbon monoxide for about 20 min. Subsequently it was placed into the spectrometer of which the sample space had been preheated to the reaction temperature, after which the reaction was monitored by means of ^1H NMR spectroscopy. During the reaction a replacement of the signal belonging to **1** by those belonging to $Ru(CO)_3(^iPr\text{-}DAB)$ [16] was observed.

*Treatment of $FeRu(CO)_5(PPh_3)(^iPr\text{-}DAB)$ (**4c**) with carbon monoxide under high pressure*

A total of 50 mg of $FeRu(CO)_5(PPh_3)(^iPr\text{-}DAB)$ (**4c**) was dissolved in 1.5 ml of C_6D_6 and syringed into the HP-NMR tube (*vide supra*). The tube was pressurized with 45 bar of carbon monoxide and subsequently placed into the spectrometer, after which the reaction was monitored by means of ^1H and ^{31}P NMR spectroscopy. The NMR data indicated a conversion of **4c** to **1b** and free triphenylphosphine.

*Hydrogenation of $FeRu(CO)_5(PPh_3)(^iPr\text{-}DAB)$ (**4c**) using high pressure NMR techniques*

A total of 40 mg of $FeRu(CO)_5(PPh_3)(^iPr\text{-}DAB)$ (**4c**) was dissolved in 1.5 ml of C_6D_6, monitored by means of ^1H NMR and subsequently syringed into the HP-NMR tube (*vide supra*). The tube was pressurized with 40 bar of hydrogen for about 75 min. Subsequently the tube was placed into the spectrometer of which the sample space had been pre-heated to 110 °C, after which the reaction was monitored by means of ^1H NMR spectroscopy. The NMR data indicated that a conversion of **4c** to **5** took place without the formation of the side product **8**.

Reaction of $Ru(CO)_3(^iPr\text{-}DAB)$, prepared in situ, with PPh_3

A total of 49.7 mg of $Ru_2(CO)_5(IAE)$ [11] (0.08 mmol) was suspended in 1.5 ml of C_6D_6 together with 105.6 mg of PPh_3 (0.40 mmol) and placed into the HP-NMR tube. The sample was pressurized with 40 bar of CO for about 15 min and subsequently the tube was placed at 100 °C for 30 min. After this period the yellow–orange suspension had turned into a dark red solution and subsequently the tube was placed into the NMR spectrometer, of which the sample space had been pre-heated to 110 °C, and the reaction was monitored by means of NMR spectroscopy. The resulting NMR data showed an initial formation of $Ru(CO)_3(^iPr\text{-}DAB)$ [16], followed by a conversion to $Ru(CO)_3(PR_3)_2$ [14] and free ^iPr-DAB.

*Crystal structure determination of $FeRu(CO)_4(PPh_3)_2(^iPr\text{-}Pyca)_2$ (**6a**)*

A brick-shaped crystal (dimensions 0.65×0.40×0.30 mm approximately) was used for data collection on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation and θ–2θ scan. A total of 7484 unique reflections was measured within the range $-13 \leqslant h \leqslant 0$, $-16 \leqslant k \leqslant 16$ and $-17 \leqslant l \leqslant 17$. Of these, 5886 were above the significance level of 2.5 $\sigma(I)$. The maximum value of $\sin\theta/\lambda$ was 0.56 Å^{-1}. Two standard reflections ($\bar{2}00$, $\bar{1}2\bar{2}$) were measured hourly; they showed a 14% decrease during the 83 hours collection time, which was corrected for. Unit-cell pa-

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*Since usually traces of condensed carbon monoxide were present on top of the reaction mixture care should be taken for pressure building up on warming of the mixture to room temperature.

**The thermal instability of $Fe_3(CO)_{12}$ in solution at temperatures above 60 °C is well established (see ref. 18).

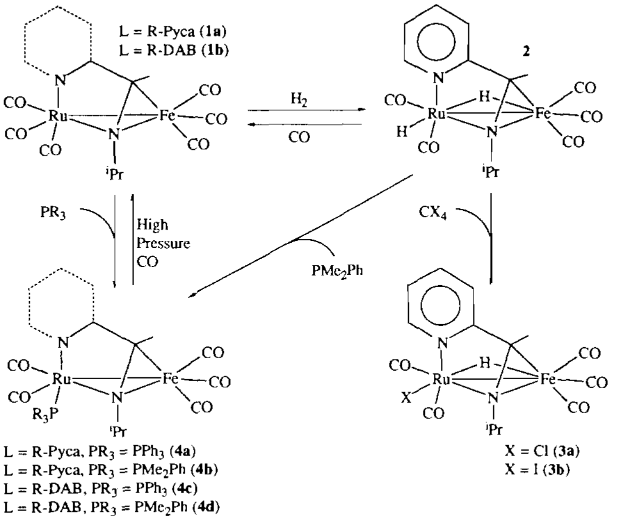
rameters were refined by a least-squares fitting procedure using 23 reflections with $80 \leq 2\theta \leq 84°$. Corrections for Lorentz and polarization effects were applied. The Fe, Ru and both P atoms were found by direct methods. The rest of the non-hydrogen atoms were located using difference Fourier maps. The H atoms were initially placed in calculated positions. Block-diagonal least-squares refinement on F, anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms, restraining the latter in such a way that the distance to their carrier remained constant at approximately 1.09 Å, converged to $R = 0.064$, $R_w = 0.097$, $(\Delta/\sigma)_{max} = 0.39$, $w = (5.98 + F_{obs} + 0.0102F_{obs}^2)^{-1}$. An empirical absorption correction (DIFABS) [19] was applied, with corrections in the range 0.711–1.498. A final difference Fourier map revealed a residual electron density between −1.1 and 1.8 e Å^{-3}. Scattering factors were taken from Cromer and Mann [20]. Anomalous dispersion for Fe and Ru was corrected for. All calculations were performed with XTAL3.0, unless stated otherwise [21].

Results and discussion

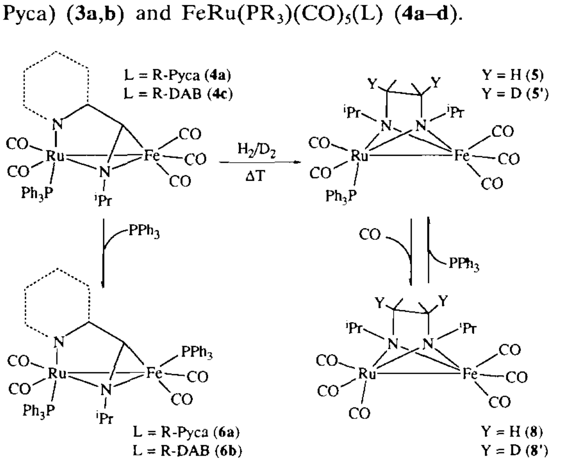
Synthesis and structures of the new complexes

$H_2FeRu(CO)_5$(^{i}Pr-Pyca) (**2**) has been prepared from $FeRu(CO)_6$(^{i}Pr-Pyca) (**1a**) and hydrogen in various solvents. The highly reactive dihydride complex **2** may exchange the terminal hydride ligand for a halide of CX_4, leading to the formation of HFeRu(X)$(CO)_5$(^{i}Pr-Pyca) (X = Cl (**3a**); I (**3b**)). Reaction of **2** with CO gave $FeRu(CO)_6$(^{i}Pr-Pyca) (**1a**), whereas **2** with PMe_2Ph afforded $FeRu(CO)_5(PMe_2Ph)$(^{i}Pr-Pyca) (**4b**). Complexes **4** could easily be prepared from the hexacarbonyl complexes $FeRu(CO)_6$(α-diimine) (α-diimine = ^{i}Pr-Pyca (**1a**); ^{i}Pr-DAB (**1b**)) by reaction with the appropriate phosphine in hexane, giving **4a–d** in high yields (more than 85%). The observed reaction sequence and the proposed structures of the various complexes, based on their spectroscopic data, are shown in Scheme 3.

Treatment of $FeRu(CO)_5(PPh)_3$(^{i}Pr-DAB) (**4c**) with hydrogen/deuterium at 110 °C yielded $FeRu(CO)_5$-(PPh_3)(^{i}Pr-N-C(H)(Y)C(H)(Y)-N-^{i}Pr) (Y = H (**5**); D (**5′**)). Complexes **5** could easily and reversibly be converted to $FeRu(CO)_6$(^{i}Pr-N-C(H)(Y)C(H)(Y)-N-^{i}Pr) (Y = H (**8**); D(**8′**)) by reaction with carbon monoxide (Scheme 4). Finally reaction of **4a** or **4c** with PPh_3 afforded the new complexes $FeRu(CO)_4(PPh_3)_2$(α-diimine) (α-diimine = ^{i}Pr-Pyca (**6a**); ^{i}Pr-DAB (**6b**)), of which only **6a** could be isolated (Scheme 4).



Scheme 3. Observed reaction sequence and proposed structures of complexes $H_2FeRu(CO)_5$(^{i}Pr-Pyca) (**2**), HFeRu(X)$(CO)_5$(^{i}Pr-Pyca) (**3a,b**) and $FeRu(PR_3)(CO)_5$(L) (**4a–d**).



Scheme 4. Preparation of complexes **5**/**5′**, **6a,b**, and **8**/**8′** from $FeRu(CO)_5(PPh_3)$(L) (L = R-Pyca (**4a**); R-DAB (**4c**)).

Molecular structure of $FeRu(CO)_4(PPh_3)_2$(^{i}Pr-Pyca)$_2$ (6a)

A view [22] of the structure and the atomic numbering is shown in Fig. 1 while Table 1 contains a selection of the bond distances and bond angles of **6a**. The structure consists of a $Ru(CO)_2(PPh_3)$ unit and a $Fe(CO)_2(PPh_3)$ unit bridged by an ^{i}Pr-Pyca ligand. The structure contains an Fe–Ru bond with a bond length of 2.645(2) Å, which is comparable to the values reported for $FeRu(CO)_6$(^{i}Pr-DAB) (2.6602(9) Å) [10] and $FeRu(CO)_6$(^{i}Pr-Pyca) (2.653(3) Å) [9]. These values are as expected for single Fe–Ru bonds which usually vary from 2.60 to 2.80 Å with the weighted average being approximately 2.69 Å [23].

In the first instance one would have expected some lengthening of the Fe–Ru bond owing to substitution of two CO ligands by two PPh_3 ligands [24–26]. However, the increased electron density on the bimetallic unit is obviously transferred to the remaining carbonyl ligands via an increased π-donation, resulting in a shortening

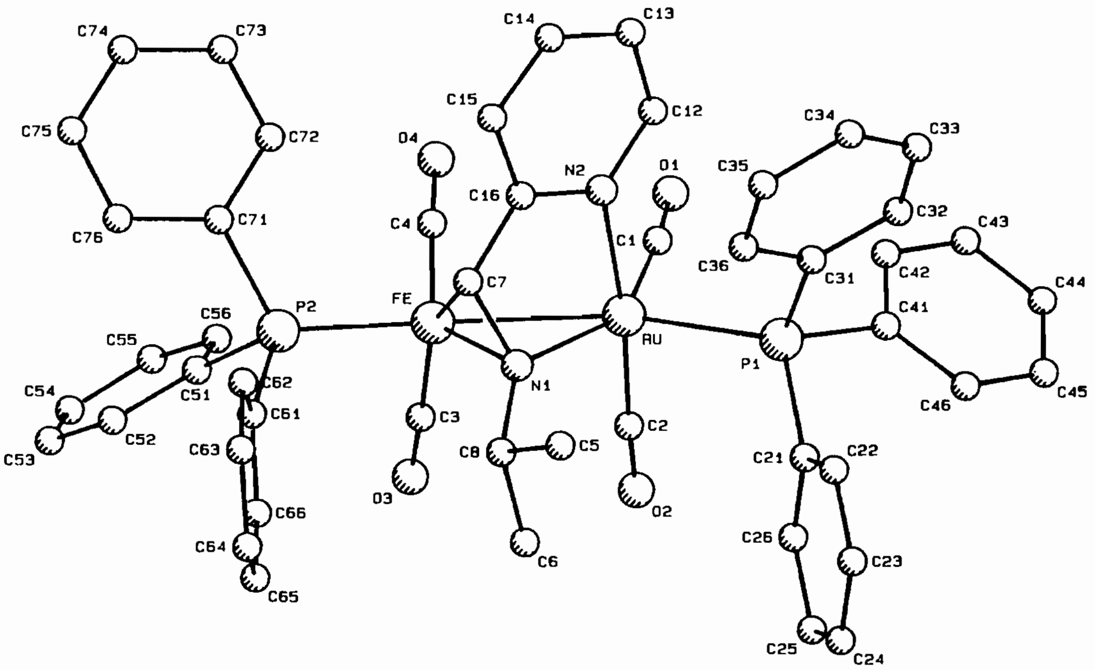


Fig. 1. Molecular structure of $FeRu(CO)_4(PPh_3)_2$(^{i}Pr-Pyca) (**6a**).

of the metal carbon distances in **6a** (Fe–CO = 1.760 Å (mean), Ru–CO = 1.855 Å (mean)) compared to $FeRu(CO)_6$(^{i}Pr-Pyca) (Fe–CO = 1.780 Å (mean), Ru–CO = 1.920 Å (mean)) [9] whereas, on the other hand, the C–O distances within **6a** (1.163 Å (mean)) are lengthened compared to those of $FeRu(CO)_6$(^{i}Pr-Pyca) (1.142 Å (mean)) [9].

The ^{i}Pr-Pyca ligand is coordinated to the Ru centre via both nitrogen atoms and to the Fe centre via coordination of an η^2-C=N bonded imine group. As a result this C(7)–N(1) imine bond is substantially elongated (1.42(1) Å) as compared to for instance the value of 1.258(3) Å in the case of free ^{c}Hex-DAB [27]. The lengthening of the η^2-coordinated C=N bond is larger for **6a** than for $FeRu(CO)_6$(^{i}Pr-Pyca) (1.393(5) Å) [9], which may be rationalized by the larger π-donation from the iron centre as a result of the substitution of two carbonyl ligands by two phosphine ligands.

The Ru–P(1) distance in **6a** is 2.412(3) Å which is normal for a triphenylphosphine ligand coordinated to a Ru(0) centre and only slightly longer than the distances observed for $Ru_3(CO)_{11}(PPh_3)$ (2.380(6) Å) [26] and for the mixed clusters $Fe_2Ru(CO)_{11}(PPh_3)$ (2.363(1) Å) [25], $FeRu_2(CO)_{11}(PPh_3)$ (2.361(2) Å) [25] and $FeRu_2(CO)_{10}(PPh_3)_2$ (2.377(3) Å) [25]. The Fe–P(2) distance in **6a** (2.195(3) Å) is relatively short compared to the Fe–P distances of, for instance, $Fe_3(CO)_{11}(PPh_3)$ (2.25 Å) [28] and $Fe(CO)_4(PPh_3)$ (2.244(1) Å) [29], indicating that the phosphine ligand is rather strongly bonded to the Fe centre.

As in the case of other heterodinuclear compounds it may be noted there is a rather severe distortion of the planarity of the σ-N,μ_2-N′,η^2-C=N′ coordinated α-diimine ligand, since the torsion angle between C(7)–N(1) and C(16)–N(2) is 22°. This value is even larger than the ones found for $FeRu(CO)_6$(^{i}Pr-DAB) (13°) [10], $HFeRu(Me)(CO)_5$(^{i}Pr-DAB) (14.2°) [30] and $FeRu(CO)_6$(^{i}Pr-Pyca) (17°) [9]. This distortion is probably caused by the difference in size between the two metal atoms.

IR spectroscopy and analyses

The IR spectroscopic data have been summarized in Table 2 together with the results of the elemental analyses. Comparison of the IR data of $FeRu(CO)_6$(^{i}Pr-Pyca) [9] with those of $FeRu(CO)_5(PPh_3)$(^{i}Pr-Pyca) (**4a**, **b**) and $FeRu(CO)_4(PPh_3)_2$(^{i}Pr-Pyca) (**6a**) showed a substantial shift to lower wavenumber, as expected, because of the substitution of two carbonyls by phosphine ligands. It should be noted that the data reported for complex **6b** were obtained from impure reaction mixtures, since a pure sample of **6b** could not be obtained.

NMR spectroscopy

The ^{1}H NMR and ^{13}C NMR spectroscopic data have been summarized in Tables 3 and 4, respectively. In the NMR spectra of uncoordinated α-diimine ligands the imine protons and the imine carbon atoms absorb in the 8–9 ppm and the 155–165 ppm regions, respectively [31]. However if an α-diimine uses the π-electrons of

TABLE 1. Selected bond distances (Å) and bond angles (°) of the non-hydrogen atoms of FeRu(CO)$_4$(PPh$_3$)$_2$(^{i}Pr-Pyca) (**6a**) (with e.s.d.s in parentheses)

Ru–Fe	2.645(2)	Ru–P1	2.412(3)	Ru–C1	1.85(1)
Ru–C2	1.86(1)	Ru–N1	2.138(8)	Ru–N2	2.111(8)
Fe–P2	2.195(3)	Fe–C3	1.77(1)	Fe–C4	1.75(1)
Fe–C7	2.05(1)	Fe–N1	1.962(9)	C1–O1	1.18(2)
C2–O2	1.15(1)	C3–O3	1.15(1)	C4–O4	1.17(1)
C5–C8	1.52(2)	C6–C8	1.52(1)	C7–C16	1.42(1)
C7–N1	1.42(1)	C8–N1	1.48(1)	C12–C13	1.40(2)
C12–N2	1.33(1)	C13–C14	1.39(2)	C14–C15	1.39(2)
C15–C16	1.41(1)	C16–N2	1.37(1)		

Fe–Ru–P1	155.61(9)	Fe–Ru–C1	103.9(5)
Fe–Ru–C2	89.4(4)	Fe–Ru–N1	47.0(3)
Fe–Ru–N2	84.6(3)	P1–Ru–C1	100.3(5)
P1–Ru–C2	94.1(4)	P1–Ru–N1	108.6(3)
P1–Ru–N2	92.0(3)	C1–Ru–C2	89.4(5)
C1–Ru–N1	149.8(5)	C1–Ru–N2	90.6(4)
C2–Ru–N1	96.8(4)	C2–Ru–N2	173.8(5)
N1–Ru–N2	80.1(3)	Ru–Fe–P2	166.3(1)
Ru–Fe–C3	98.3(4)	Ru–Fe–C4	89.7(4)
Ru–Fe–C7	73.9(3)	Ru–Fe–N1	52.8(2)
P2–Fe–C3	90.2(4)	P2–Fe–C4	99.2(4)
P2–Fe–C7	93.2(3)	P2–Fe–N1	114.3(3)
C3–Fe–C4	101.1(5)	C3–Fe–C7	147.7(5)
C3–Fe–N1	108.8(5)	C4–Fe–C7	110.0(5)
C4–Fe–N1	134.2(5)	C7–Fe–N1	41.4(4)
Ru–C1–O1	175(1)	Ru–C2–O2	175(1)
Fe–C3–O3	177(1)	Fe–C4–O4	176(1)
Fe–C7–C16	114.4(8)	Fe–C7–N1	65.9(5)
C16–C7–N1	118.5(9)	C5–C8–C6	111(1)
C5–C8–N1	109.9(8)	C6–C8–N1	111.0(9)
C13–C12–N2	123(1)	C12–C13–C14	118(1)
C13–C14–C15	120(1)	C14–C15–C16	119(1)
C7–C16–C15	123(1)	C7–C16–N2	116.0(9)
C15–C16–N2	120.9(9)	Ru–N1–Fe	80.2(3)
Ru–N1–C7	105.2(6)	Ru–N1–C8	136.9(7)
Fe–N1–C7	72.7(6)	Fe–N1–C8	124.9(7)
C7–N1–C8	115.2(8)	Ru–N2–C12	128.9(8)
Ru–N2–C16	112.0(6)	C12–N2–C16	119.0(9)

a C=N moiety for coordination the resonances of both the imine proton and the imine carbon atoms are shifted drastically to lower frequency, owing to the π-backbonding from the metal to the η^2-bonded imine moiety. A similar shift is observed in the NMR spectra of complex **2** which show the characteristic features of a 6e donating σ-N,μ_2-N′,η^2-C=N′ coordinated Pyca ligand (imine proton at 3.43 ppm and imine carbon atom around 65 ppm). In addition to the signals belonging to the ^{i}Pr-Pyca ligand the ^{1}H NMR of **2** also shows doublets at −7.01 and −15.17 ppm indicating that two hydride atoms are present in **2**. From the chemical shift values it may be concluded that one of the hydrides occupies a terminal (−7.01 ppm) and the other hydride a bridging (−15.17 ppm) position.

The carbonyl region of the ^{13}C NMR spectrum of **2** shows one signal for the carbonyls coordinated to iron, indicating a rapid scrambling on the NMR timescale which has also been reported for several other systems containing Fe–carbonyl ligands [9, 10, 32, 33]. The Ru–carbonyl region shows only two signals instead of three as in the case of starting complex **1a**, which implies the presence of two carbonyls on Ru.

A proposed structure for **2**, based on the NMR data, is shown in Scheme 3. The small coupling observed between the hydride signal at −15.17 ppm and the signal of proton of the η^2-coordinated imine moiety is in agreement with the bridging position of this hydride.

Both the ^{1}H and the ^{13}C NMR of the complexes **3a,b** (Scheme 3) show the characteristic features of a Pyca ligand in a 6e donating σ-N,μ_2-N′,η^2-C=N′ coordination mode with the imine protons resonating around 4.2 ppm, while the corresponding carbon atoms were observed around 67 ppm. In contrast to **2** complexes **3a,b** contain only one hydride atom which, as concluded from the chemical shift, is bridging. The coupling between this bridging hydride and the proton of the η^2-coordinated imine moiety is smaller for complexes **3a,b** (<0.5 Hz) than for **2**.

Complexes **4a–d** show the characteristic features of an α-diimine ligand in a 6e donating σ-N,μ_2-N′,η^2-C=N′ coordination mode, dominated by the low frequency shift of the η^2-coordinated part of the ligand (*vide supra*). Complexes **4c,d** also show ^{1}H NMR signals of a σ-bonded imine moiety around 7.75 ppm whereas the ^{13}C NMR signals of the corresponding carbon atoms are observed around 170 ppm [9, 10, 31, 34]. The carbonyl regions of the ^{13}C NMR spectra of **4a–d** show one signal for the carbonyls coordinated to iron whereas the carbonyl ligands coordinated to ruthenium appear as separate signals. Since only two carbonyls coordinated to ruthenium are observed, both with a phosphorus coupling, we conclude that the phosphine is coordinated to the ruthenium centre.

Both the ^{1}H NMR and the ^{13}C NMR of complex **5** show signals belonging to a N–CH$_2$CH$_2$–N moiety. The C$_2$H$_4$ moiety appears in the ^{1}H spectrum as two sets of double doublets both with an intensity of two protons, resulting from the inequivalence of the iron-side and the ruthenium-side of the C$_2$H$_4$ fragment. The carbonyl region of the ^{13}C NMR spectrum shows three signals at 205.8, 206.7 and 216.1 ppm, respectively, with relative intensities of 1:2:2. All three signals appear as doublets due to a coupling with the phosphorus atom. From the observed fluxional behaviour (*vide infra*) it was concluded that the signals at 205.8 and 216.1 ppm belong to carbonyl ligands coordinated to the iron centre. The relatively large coupling between the phosphorus atom at the Fe centre and the Fe–carbonyl at 205.8 ppm suggests that these two ligands are *trans* to each other. We therefore propose a staggered geometry of the Fe(CO)$_3$ unit and the Ru(CO)$_2$(PPh$_3$) unit with respect to each other, while the sterically demanding phosphine

TABLE 2. IR data and elemental analyses of the complexes **2**, **3a**,**b**, **4a–d**, **5**, **6a**,**b** and **7**

Complex	IR ν(C=O) (cm^{-1})	Elemental analysis: obs. (calc.) (%)		
		C	H	N
2[a]	2059(s), 2026(vs), 1987(vs), 1981(s), 1966(s)	not analyzed[g]		
3a[b]	2071(s), 2044(s), 1998(s), 1987(sh)	34.91 (34.91)	2.80 (2.72)	5.80 (5.82)
3b[c]	2068(s), 2042(s), 2002(s), 1988(m)	29.34 (29.34)	2.34 (2.29)	4.84 (4.89)
4a[d]	2023(vs), 1979(vs), 1953(s), 1920(m)	53.59 (54.33)	3.74 (3.85)	3.90 (3.96)
4b[d]	2022(vs), 1973(vs), 1953(s), 1908(m)	44.40 (45.30)	3.25 (3.21)	4.73 (4.80)
4c[d]	2021(vs), 1975(vs), 1947(s), 1914(m)	53.01 (53.23)	4.56 (4.47)	4.08 (4.00)
4d[d]	2023(vs), 1975(vs), 1952(s), 1914(m)	43.76 (43.84)	4.82 (4.73)	4.78 (4.87)
5[d]	2032(s), 1983(vs), 1960(s), 1947(m), 1923(w)	52.90 (53.08)	4.83 (4.74)	4.09 (3.99)
6a[b,f]	1995(vs), 1932(s), 1913(m), 1862(m)	62.10 (62.25)	5.36 (4.84)	2.93 (2.68)
6a[e]	1995(vs), 1930(s), 1908(m), 1865(m)			
6b[e]	2000(vs), 1934(s), 1918(m), 1868(m)	not isolated		
7[b]	2048(s), 2005(vs), 1975(m), 1955(sh), 1925(w)	not isolated		

[a] Hexane solution. [b] CH_2Cl_2 solution. [c] Hexane/CH_2Cl_2 (1/1). [d] Hexane/CH_2Cl_2 (9/1). [e] Toluene solution. [f] Calculated values comprise one equivalent of THF. [g] No analytically pure sample could be obtained for this compound.

TABLE 3. ^{1}H NMR data[a] of the complexes **2**, **3a**,**b**, **4a–d**, **5** and **6a**

2[b]	7.64 (1H, d, 5 Hz, py-H6); 6.30 (2H, m, py-H3/H4); 5.68 (1H, dd, 7 Hz/5 Hz, py-H5); 3.43 (1H, d, 1.2 Hz, η^2-N=CH); 2.39 (1H, sept, 6.5 Hz, ^{i}Pr-CH); 1.37/1.20 (3H/3H, d, 6.5 Hz, ^{i}Pr-CH_3); −7.01 (1H, d, 16 Hz, Ru-H; −15.17 (1H, dd, 16 Hz/1.2 Hz, μ-H)
3a[c]	8.19 (1H, d, 5 Hz, py-H6); 7.55 (2H, m, py-H3/H4); 7.00 (1H, dd, 7 Hz/5 Hz, py-H5); 4.14 (1H, s, η^2-N=CH); 3.39 (1H, sept, 6.5 Hz, ^{i}Pr-CH); 1.73/1.62 (3H/3H, d, 6.5 Hz, ^{i}Pr-CH_3); −22.07 (1H, s, μ-H)
3b	8.29 (1H, d, 5 Hz, py-H6); 7.53 (1H, dd, 7 Hz/4 Hz, py-H4); 7.27 (1H, d, 4 Hz, Py-H3) 6.94 (1H, dd, 7 Hz/5 Hz, py-H5); 4.19 (1H, s, η^2-N=CH); 3.18 (1H, sept, 6.4 Hz, ^{i}Pr-CH); 1.79/1.73 (3H/3H, d, 6.4 Hz, ^{i}Pr-CH_3); −19.46 (1H, s, μ-H)
4a	7.35–6.80 (18H, m, P-C_6H_5+Py-H3/H4/H6); 5.93 (1H, dd, 7 Hz/5 Hz, py-H5); 3.86 (1H, s, η^2-N=CH); 3.12 (1H, sept, 6 Hz, ^{i}Pr-CH); 1.05/0.91 (3H/3H, d, 6 Hz, ^{i}Pr-CH_3)
4b	7.40–6.95 (8H, m, P-C_6H_5+Py-H3/H4/H6); 6.36 (1H, dd, 7 Hz/5 Hz, py-H5); 3.88 (1H, s, η^2-N=CH); 3.31 (1H, sept, 6.7 Hz, ^{i}Pr-CH); 1.95/1.86 (3H/3H, d, 9 Hz, P-CH_3); 1.30/1.24 (3H/3H, d, 6.7 Hz, ^{i}Pr-CH_3)
4c	7.77 (1H, d, 1 Hz, σ-N=CH); 7.50–7.20 (15H, m, P-C_6H_5); 3.63 (1H, d, 1 Hz, η^2-N=CH); 3.36/2.62 (1H/1H, sept, 6 Hz, ^{i}Pr-CH); 1.07/1.03/0.30 (3H/6H/3H, d, 6 Hz, ^{i}Pr-CH_3)
4d	7.76 (1H, d, 2 Hz, σ-N=CH); 7.55–7.45 (5H, m, P-C_6H_5); 3.88 (1H, d, 2 Hz, η^2-N=CH); 3.37/2.96 (1H, sept, 6.5 Hz, ^{i}Pr-CH); 1.94/1.90 (3H/3H, d, 8.8 Hz, P-CH_3); 1.31/1.26/1.08/0.82 (3H/3H/3H/3H, d, 6.5 Hz, ^{i}Pr-CH_3)
5	7.80–7.30 (15H, m, P-C_6H_5); 3.39 (2H, sept, 6.4 Hz, ^{i}Pr-CH); 2.61/2.20 (2H/2H, dd, 6.6 Hz/2 Hz, N-CH_2CH_2N); 1.30/0.88 (6H/6H, d, 6.4 Hz, ^{i}Pr-CH_3)
6a[d]	7.75–7.60 (6H, m, P-C_6H_5); 7.35–7.20 (24H, m, P-C_6H_5); 7.05 (1H, dd, 6 Hz/6 Hz, py-H4); 6.96 (1H, d, 5 Hz, py-H6); 6.49 (1H, d, 6 Hz, Py-H3); 5.88 (1H, dd, 6 Hz/5 Hz, py-H5); 2.86 (1H, d, 14.1 Hz, η^2-N=CH); 1.59 (1H, sept, 6 Hz, ^{i}Pr-CH); 0.73/0.59 (3H/3H, d, 6 Hz, ^{i}Pr-CH_3)

[a] In $CDCl_3$ solution at 100 MHz unless stated otherwise. [b] C_6D_6 solution. [c] CD_2Cl_2 solution. [d] 300 MHz.

points away from the hydrogenated DAB ligand (Fig. 2).

At higher temperatures the three carbonyl ligands at the iron centre become involved in a scrambling process leading to a broadening of the signals at 205.8 and 216.1 ppm, starting at about 263 K. At a temperature of 373 K (toluene-d_8 solution) the scrambling carbonyls give rise to a broad signal at about 213 ppm, which is close to the weighted average of the two signals in the slow exchange limit (212.7 ppm). At higher temperatures a decomposition of the complex prevented reaching the fast exchange limit completely.

When using deuterium both the signals belonging to the iron-side of the C_2 moiety and the signals belonging to the ruthenium-side of the C_2 moiety showed a relative intensity of one proton. Both in complex **5** and complex

TABLE 4. ^{13}C NMR data[a] of the complexes **2**, **3a**,**b**, **4a–d**, **5** and **6a**

2[b]	26.1/29.4 ($^iPr-CH_3$); 67.1/68.5 ($^iPr-CH + \eta^2-N{=}CH$); 118.2 (py-C^5); 119.6 (py-C^3); 136.9 (py-C^4); 151.6 (py-C^6); 170.5 (py-C^2); 200.4/203.3 (Ru-CO); 215.7 (Fe-CO)
3a[c]	25.6/27.2 ($^iPr-CH_3$); 68.0/68.7 ($^iPr-CH + \eta^2-N{=}CH$); 119.5 (py-C^5); 121.7 (py-C^3); 138.8 (py-C^4); 151.6 (py-C^6); 168.5 (py-C^2); 195.5/196.7 (Ru-CO); 204.1/208.2/211.3 (Fe-CO)
3b	25.6/30.0 ($^iPr-CH_3$); 67.8/69.5 ($^iPr-CH + \eta^2-N{=}CH$); 118.9 (py-C^5); 121.6 (py-C^3); 138.5 (py-C^4); 152.6 (py-C^6); 168.4 (py-C^2); 195.3/196.8 (Ru-CO); 203.5/207.9/211.1 (Fe-CO)
4a	25.3/27.2 ($^iPr-CH_3$); 67.2 (^iPr-CH); 65.4 ($\eta^2-N{=}CH$); 116.0 (py-C^5); 117.4 (py-C^3); 128.9 (d, 9.6 Hz, Ph-C3/C5); 130.5 (d, 1.8 Hz, Ph-C4); 133.3 (d, 11.2 Hz, Ph-C2/C6); 133.4 (d, 35.9 Hz, Ph-C1); 136.1 (py-C^4); 150.7 (py-C^6); 172.0 (py-C^2); 203.5 (d, 7 Hz, Ru-CO); 209.8 (Ru-CO); 217.3 (Fe-CO)
4b	17.4 (d, 6.9 Hz, P-CH_3); 18.4 (d, 9.8 Hz, P-CH_3); 27.9/25.4 ($^iPr-CH_3$); 67.0 (^iPr-CH); 64.7 ($\eta^2-N{=}CH$); 117.0 (py-C^5); 117.9 (py-C^3); 129.6 (d, 9.6 Hz, Ph-C3/C5); 130.1 (d, 2 Hz, Ph-C4); 129.3 (d, 9.7 Hz, Ph-C2/C6); 137.1 (d, 37.9 Hz, Ph-C1); 136.8 (py-C^4); 150.2 (d, 2 Hz, py-C^6); 172.8 (py-C^2); 202.8 (d, 7.9 Hz, Ru-CO); 208.5 (d, 4.2 Hz, Ru-CO); 219.1 (Fe-CO)
4c	21.8/23.6/24.8/28.1 ($^iPr-CH_3$); 63.8/67.3 (^iPr-CH); 60.8 ($\eta^2-N{=}CH$); 129.1 (d, 9.6 Hz, Ph-C3/C5); 130.9 (d, 2.1 Hz, Ph-C4); 133.8 (d, 11.2 Hz, Ph-C2/C6); 134.3 (d, 36 Hz, Ph-C1); 136.1 (py-C^4); 171.1 ($\sigma-N{=}CH$); 203.4 (d, 6 Hz, Ru-CO); 209.9 (d, 2 Hz, Ru-CO); 218.7 (Fe-CO)
4d[d]	18.5 (d, 3.3 Hz, P-CH_3); 19.5 (d, 3 Hz, P-CH_3); 22.3/23.7/25.5/28.0 ($^iPr-CH_3$); 67.3/64.4 (^iPr-CH); 57.5 ($\eta^2-N{=}CH$); 129.3 (d, 10.5 Hz, Ph-C3/C5); 130.2 (d, 2.5 Hz, Ph-C4); 129.8 (d, 11 Hz, Ph-C2/C6); 138.6 (d, 36.1 Hz, Ph-C1); 171.4 ($\sigma-N{=}CH$) 219.6 (Fe-CO)
5[e]	23.8/23.9/24.6/24.7 ($^iPr-CH_3$); 51.8 (br, N-CH_2CH_2-N); 64.4/64.6 (^iPr-CH); 128.8 (d, 9.1 Hz, Ph-C3/C5); 130.3 (d, 2 Hz, Ph-C4); 133.8 (d, 14.3 Hz, Ph-C2/C6); 136.9 (d, 32.5 Hz, Ph-C1); 205.8 (d, 14.3 Hz, Fe-CO); 206.7 (d, 5.3 Hz, Ru-CO); 216.1 (d, 4.5 Hz, Fe-CO)
6a[f]	26.0/26.8 ($^iPr-CH_3$); 63.3 (br, ^iPr-CH); 70.2 (d, 20 Hz, $\eta^2-N{=}CH$); 115.1 (py-C^5); 116.3 (py-C^3); 128.4–134.0 (m, Ph-C2/C3/C4/C5/C6); 135.5/138.2 (d, 32.5 Hz,/36.7 Hz, Ph-C1); 132.7 (py-C^4); 151.5 (py-C^6); 172.6 (py-C^2); 205.0/212.7 (Ru-CO); 218.6/228.7 (Fe-CO)

[a] $CDCl_3$ solution, 263 K unless stated otherwise. [b] C_6D_6 solution, 293 K. [c] CD_2Cl_2 solution. [d] Ru-CO not observed. [e] 243 K. [f] 233 K, $Cr(Acac)_3$.

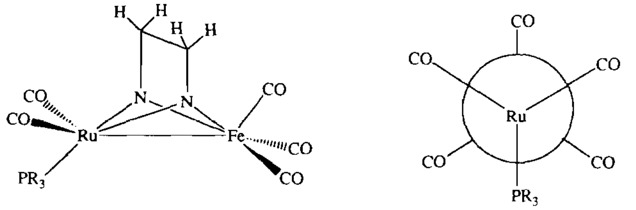


Fig. 2. Proposed structure of complex 5.

8 these signals appeared as doublets ($J = 3.7$ Hz), broadened by deuterium coupling. The presence of these two chemically inequivalent protons in the deuterated complexes **5** and **8** together with the observed coupling constant clearly points towards a *trans* addition of D_2 to the central C–C bond of the DAB ligand, analogous to $FeRu(CO)_6(^iPr-N-C(H)(D)C(H)(D)-N-^iPr)$ [6] (Scheme 2) and $FeMn(CO)_6(H)(pTol-N-C(H)(D)C(H)(D)-N-pTol)$ (Scheme 1, structure **a**) [7].

The presence of a Pyca ligand in a 6e donating σ-N,μ_2-N',η^2-C=N' coordination mode in **6a** (Scheme 4) is shown both by the ^1H NMR spectrum (η^2-coordinated imine proton at 2.86 ppm) and the ^{13}C NMR spectrum (corresponding carbon atom at 70.2 ppm). Both the imine proton and the imine carbon atom appear as a doublet due to a coupling with the phosphine on the iron atom. The observed coupling constants for the imine carbon atom (20 Hz) and for the imine proton atom (14.1 Hz) are rather large, which is unexpected since the phosphine and the imine moiety are positioned *cis* to each other (P(1)FeC(7) = 93.2(3)°). Since both the imine moiety and the phosphine appear to be strongly coordinated to the iron centre, it is probably the strength of these bonds which cause the large coupling.

The two phosphine ligands appear as two doublets ($J = 22$ Hz) in the ^{31}P NMR spectrum at 23.4 and 74.5 ppm, respectively ($CDCl_3$; 120 MHz). The carbonyl region of the ^{13}C NMR spectrum of the complex shows four signals varying from 205.0 to 228.7 ppm. No phosphorus coupling could be detected on these carbonyl ligands, which is probably due to the *cis* arrangement of all four carbonyl ligands with respect to the phosphine ligand (P–M–CO angles vary from 90.2 to 100.3°). The use of $Cr(Acac)_3$ did lead to a broadening of all signals, so that the (probably small) phosphorus coupling on the carbonyl ligands could not be detected.

The value of 228 ppm is at rather low field for a terminal carbonyl ligand, which might indicate the presence of a bridging carbonyl ligand in solution. However IR spectroscopy showed that the structure in solution is similar to the structure in the solid state. We therefore suggest that this low field value is caused by a large amount of π-donation to the carbonyl ligands as a result of the increase of electron density due to the two phosphine ligands on the bimetallic core.

Synthesis of $H_2FeRu(CO)_5(^iPr\text{-}Pyca)$ (2) and reactivity of 2 vs. CX_4, CO and PR_3

$FeRu(CO)_6(^iPr\text{-}Pyca)$ (**1a**) reacts with hydrogen to give the novel and highly reactive species $H_2FeRu(CO)_5(^iPr\text{-}Pyca)$ (**2**) resulting from an oxidative addition accompanied by a substitution of a carbonyl ligand (Scheme 3). The reaction can be performed either thermally (85 °C) under one atmosphere of hydrogen, or by treatment of the starting complex with Me_3NO in the presence of hydrogen. When using the thermal route it was found that it is important to refresh the hydrogen atmosphere regularly in order to remove the liberated carbon monoxide. This can easily be understood since carbon monoxide was found to react directly with **2** to form **1a**.

Upon treatment of **2** with CX_4 (X = Cl, I) a rapid H/X exchange took place leading to the formation of $HFeRu(X)(CO)_5(^iPr\text{-}Pyca)$ (X = Cl (**3a**); I (**3b**)) (Scheme 3).

The high reactivity of the hydride complex $H_2FeRu(CO)_5(^iPr\text{-}Pyca)$ (**2**) is illustrated by reaction with carbon monoxide or phosphines. In both cases facile conversion was observed based on a reductive elimination of dihydrogen together with addition of the added ligand, giving $FeRu(CO)_6(^iPr\text{-}Pyca)$ (**1a**) and $FeRu(CO)_5(PMe_2Ph)(^iPr\text{-}Pyca)$ (**4b**), respectively (Scheme 3).

Complexes $FeRu(CO)_5(PR_3)(\alpha\text{-diimine})$ (α-diimine = ^{i}Pr-Pyca, $PR_3 = PPh_3$ (**4a**); α-diimine = ^{i}Pr-Pyca, $PR_3 = PMe_2Ph$ (**4b**); α-diimine = ^{i}Pr-DAB, $PR_3 = PPh_3$ (**4c**); α-diimine = ^{i}Pr-DAB, $PR_3 = PMe_2Ph$ (**4d**)) can also be prepared by treatment of the corresponding hexacarbonyl complexes (**1a,b**) with phosphines at room temperature (Scheme 3). Whereas these reactions in hexane solution reached completion within 30 min it was found that reaction times of more than 3 h were required when CH_2Cl_2 or benzene was employed as solvent. The reaction in CH_2Cl_2 or benzene could be accelerated by bubbling a continuous stream of nitrogen through the reaction mixture. It therefore seems to be necessary to remove at least one of the reaction products (i.e. CO) to reach a complete conversion rapidly. This observation indicates the existence of an equilibrium between **4** + CO and **1** + PR_3, which assumption has been ascertained, since treatment of **4c** with 45 bar of CO in a C_6D_6 solution showed a conversion from **4c** to **1b** at room temperature, reaching completion in about 2 h. After release of the CO pressure **1b** slowly reconverted to **4c**, which reaction could be accelerated by bubbling N_2 through the solution for about 15 min.

Hydrogenation of the central C–C bond of ^iPr-DAB in $FeRu(CO)_5(PPh_3)(^iPr\text{-}DAB)$ (4c)

In order to compare the reactivity of **4c** with that of $FeRu(CO)_6(^iPr\text{-}DAB)$ (**1b**) [6], **4c** was treated with hydrogen at 110 °C in toluene, resulting in the formation of $FeRu(CO)_5(PPh_3)(^iPr\text{-}N\text{-}CH_2CH_2\text{-}N\text{-}^iPr)$ (**5**) together with some side product $FeRu(CO)_6(^iPr\text{-}N\text{-}CH_2CH_2\text{-}N\text{-}^iPr)$ (**8**) (Scheme 4). Although the amount of **8** produced obviously decreased when hydrogen was bubbled through the solution instead of stirring the reaction mixture under an atmosphere of hydrogen, the yield of **8** remained at least 5% in all cases. When deuterium was used instead of hydrogen NMR spectroscopy showed a *trans* addition of D_2 to the DAB ligand, both for **5′** and **8′** (Scheme 4), in agreement with earlier reports [6, 7].

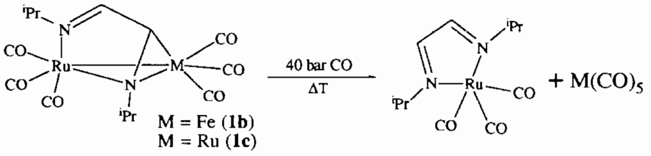
The hydrogenation reaction has also been monitored by means of high pressure NMR techniques (see 'Experimental'). Using a temperature of 100 °C and a pressure of 40 bar of hydrogen a rapid conversion of **4c** to **5** was observed, reaching completion in about 3 h. It is interesting to note that under these conditions no formation of **8** was observed.

In this respect it should be noted that already at a temperature of 60 °C **5** may be converted to **8**, while at 110 °C this reaction is very facile (Scheme 4). It is clear that during the hydrogenation reaction carbon monoxide was formed owing to some decomposition, which is the cause of the formation of **8**, even when a continuous stream of hydrogen is used to purge the solution. However, under the conditions used during the HP-NMR experiment (only 3 h at 100 °C), the amount of decomposition is probably much smaller, thus explaining the absence of the side product **8** in the reaction mixture.

In order to probe the reactive coordination site at the start of the hydrogenation process we carried out hydrogenation experiments in the presence of CO and PR_3. From 'Experimental' it is clear that CO and PR_3, respectively, completely inhibit the hydrogenation reaction. Whereas the samples of the reaction without free PPh_3 showed a normal conversion of **4c** to **5** and traces of **8**, reaching completion in about 9 h, the results of the reaction in the presence of free triphenylphosphine showed that no hydrogenation took place, but instead the formation of

$FeRu(CO)_4(PPh_3)_2(^iPr\text{-}DAB)$ (**6b**), together with substantial decomposition and formation of $Ru(CO)_3(PPh_3)_2$ [14]. Complex **6b** could therefore unfortunately not be isolated, but the analogous complex **6a** could be isolated since in this case the subsequent decomposition was less severe. According to IR data complex **4a** can be converted to **6a** in about 40 to 50% before the formation of $Ru(CO)_3(PPh_3)_2$ becomes important, and subsequent purification of the reaction mixture gave **6a**, in relatively low yields.

In order to gain more information about the inhibiting effect of coordinating ligands on the hydrogenation reactions some high pressure CO experiments were performed. Treatment of $MRu(CO)_6(^iPr\text{-}DAB)$ (M = Fe (**1b**); Ru (**1c**)) with carbon monoxide at elevated temperatures yielded the monomeric complexes $Ru(CO)_3(^iPr\text{-}DAB)$ [16] and $M(CO)_5$ (M = Fe, Ru) (Scheme 5). It should be noted that **1b** is more stable towards carbon monoxide than **1c**, as can be seen from the reaction times needed to reach complete conversion (16 h at 373 K for **1b** versus 90 min at 353 K for **1c**), which implies that the strength of the metal–η^2-C=N bond is an important factor for the course of these reactions [10]. These reactions support our assumption that under the conditions used for the hydrogenation reactions an open site may be created by rupture of the metal–η^2-C=N bond.

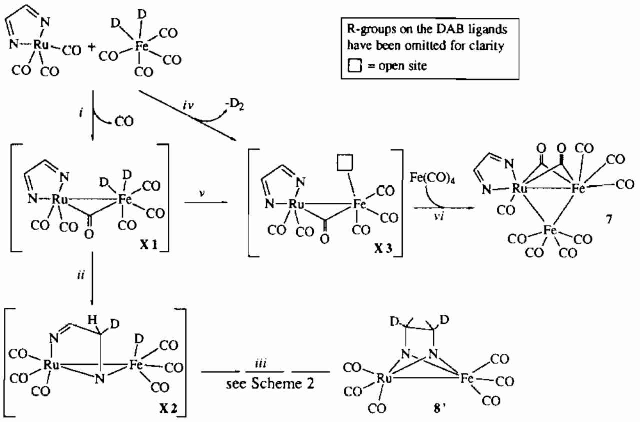


Scheme 5. Reaction of $MRu(CO)_6(^iPr\text{-}DAB)$ (M = Fe (**1b**); Ru (**1c**)) with carbon monoxide at high pressure and elevated temperatures.

Reaction of $Ru(CO)_3(^iPr\text{-}DAB)$ with $H_2Fe(CO)_4$

A key reaction involves the formation of $FeRu(CO)_6(^iPr\text{-}N\text{-}CH_2CH_2\text{-}N\text{-}^iPr)$ (**8**) from $Ru(CO)_3(^iPr\text{-}DAB)$ [16] with $H_2Fe(CO)_4$, which produces as a minor side product the new complex $Fe_2Ru(CO)_{10}(^iPr\text{-}DAB)$ (**7**)*. Complex **7** could not be isolated in a pure form due to decomposition during column chromatography. Furthermore, **7** easily converts to the very stable $FeRu(CO)_6(^iPr\text{-}DAB)$ (**1a**), the reaction being similar to the facile thermal conversion of $Fe_2Ru(CO)_{10}$(R-Pyca) to $FeRu(CO)_6$(R-pyca) [9].

It is rather intriguing to note that the starting compounds for the formation of **8** involve a 4e σ-N, σ-N′ coordinated DAB ligand bonded to ruthenium, while the hydride atoms are situated on $H_2Fe(CO)_4$. This reaction struck us as being very reminiscent of the hydrogenation of the 4e σ-N, σ-N′ coordinated DAB ligand in $Mn(Br)(CO)_3(^pTol\text{-}DAB)$. This complex was converted with three equivalents of $HFe(CO)_4^-$ to (μ-H)$FeMn(CO)_6(^pTol\text{-}N\text{-}CH_2CH_2\text{-}N\text{-}^pTol)$, whereas the use of $DFe(CO)_4^-$ led to a *trans* addition of two D atoms to the central C–C bond of the DAB ligand [7] (Scheme 1, structure **a**). In view of this similarity we propose for the system studied here the reaction scheme shown in Scheme 6.



Scheme 6. Proposed reaction scheme for the reaction of $Ru(CO)_3$(DAB) with $D_2Fe(CO)_4$.

The first step (i) probably involves the loss of CO from $D_2Fe(CO)_4$, after which $D_2Fe(CO)_3$ may react with $Ru(CO)_3(^iPr\text{-}DAB)$ to form intermediate **X1**. Successive transfer of the deuteride atoms may proceed similarly to the process shown in Scheme 2 [6], since the use of $D_2Fe(CO)_4$ gave *trans* addition of the two D atoms to the central C–C bond. It should be noted that we are still speculating about the intermediate steps of this process. For the transfer of the first deuteride atom to the DAB ligand, i.e. reaction ii, the most attractive description involves a single electron transfer mechanism [7, 8], as shown in Scheme 1.

Finally we still have to explain the formation of the trinuclear complex **7**. Since the reaction mixture contains $Fe(CO)_4$ fragments, as clearly evidenced by the formation of $Fe_3(CO)_{12}$, it might very well be that intermediate **X3** [10] is formed, either by direct reaction (iv) of $Ru(CO)_3(^iPr\text{-}DAB)$ and $Fe(CO)_4$ [10] or via intermediate **X1** (i and v). Subsequent reaction with a second $Fe(CO)_4$ fragment gives **7** (Scheme 6; reaction vi), as proposed earlier for the preparation of $Fe_2Ru(CO)_{10}$(R-Pyca) [9].

One might wonder about reactions involving other combinations, i.e. $Fe(CO)_3(^iPr\text{-}DAB)$ [35, 36] with $H_2Fe(CO)_4$, $Ru(CO)_3(^iPr\text{-}DAB)$ with $H_2Ru(CO)_4$ and $Fe(CO)_3(^iPr\text{-}DAB)$ with $H_2Ru(CO)_4$. In the first case formation of $Fe_2(CO)_6(^iPr\text{-}DAB)$ [37] occurred, while in the second case traces of $Ru_2(CO)_6(^iPr\text{-}DAB)$ were

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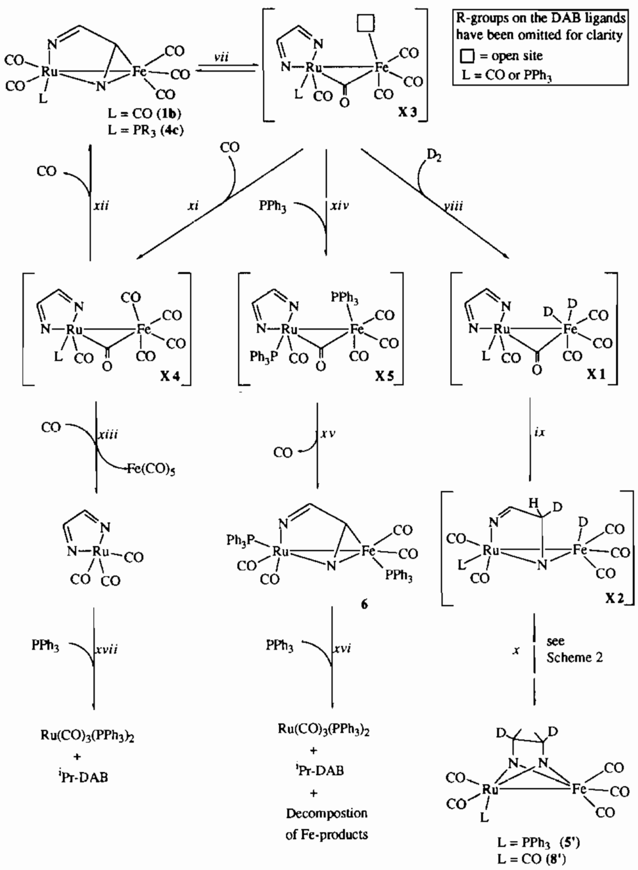
*Complex 7 has been characterized by a comparison of its spectroscopic data and its thermal reactivity with those of $Fe_2Ru(CO)_{10}$(R-Pyca). This isostructural complex has been extensively studied and discussed in a separate article (see ref. 9).

detected together with unreacted Ru(CO)$_3$(^{i}Pr-DAB). Finally, in the third case hardly any reaction was observed at all, and besides Fe(CO)$_3$(^{i}Pr-DAB) and traces of Ru$_3$(CO)$_{12}$ only decomposition was observed. However, in no instance was any hydrogenated complex observed.

Possible mechanism for the hydrogenation of complexes 1b and 4c

The proposed mechanism is shown in Scheme 7.



Scheme 7. Proposed mechanism for the hydrogenation of **1b** and **4c**.

Since the hydrogenation is completely blocked by CO and PR$_3$ the first step very likely involves the formation of an open coordination site. In previous work [6] we suggested the (partial) rupture of the Fe–Ru bond (Scheme 2) and not dissociation of a CO, since both starting compound and product, obtained in very good yield, each contained six CO groups. In view of our findings in the case of the reaction of Ru(CO)$_3$(^{i}Pr-DAB) and H$_2$Fe(CO)$_4$ (Scheme 6), the results of the treatment of **1b,c** with high-pressure carbon monoxide (Scheme 5), and the recent observation that the Fe–Ru bond is relatively a very strong one, we now tend to the assumption that the empty coordination site is created by rupture of the Fe–η^2-C=N bond, which is thermally induced as the hydrogenation always requires temperatures of about 90 °C. In the first step of the reaction scheme (vii) this leads to the formation of intermediate **X3**, which probably is in a rapid equilibrium with the starting compound **1c** or **4c**. This coordinatively unsaturated species **X3** may now further react with H$_2$ (or D$_2$) (viii) to give **X1**. From **X1** the reaction sequence may follow reported routes (Scheme 2), leading to a *trans* addition of D$_2$ and the formation of **5′** and **8′**, respectively.

In the presence of CO and PR$_3$ the reduction pathway is completely blocked and other routes become available. Reaction of **X3** with CO probably produces intermediate **X4** (xi) which may react back to **1b** or **4c** (xii). When higher CO pressures are used **X4** may react with another molecule of CO to form Ru(CO)$_3$(^{i}Pr-DAB) and Fe(CO)$_5$ (xiii) (compare Scheme 5). Since under high CO pressures **4c** easily converts to **1b** and free triphenylphosphine (Scheme 3), treatment of **4c** with high pressure carbon monoxide also leads to the formation of Ru(CO)$_3$(^{i}Pr-DAB) and Fe(CO)$_5$, via an initial conversion of **4c** to **1b** (see also Scheme 3).

In the presence of PR$_3$ intermediate **X3** will produce very likely intermediate **X5** which may then react to the new compound **6**, which with excess of PPh$_3$ leads to decomposition with the formation of Ru(CO)$_3$(PPh$_3$)$_2$ [14] and free ^{i}Pr-DAB. At first site the formation of Ru(CO)$_3$(PPh$_3$)$_2$ from **6** seems a rather complicated reaction, since analogous to reaction xiii the initial formation of the monomeric complexes Ru(CO)$_2$(PPh$_3$)(^{i}Pr-DAB) and Fe(CO)$_2$(PPh$_3$)$_3$ would be expected. However, both the thermal instability [38] and the high reactivity [39] of Fe(CO)$_2$(PPh$_3$)$_3$ are well established and explain the large amount of decomposition that is observed in this reaction. Analogous to Ru(CO)$_3$(^{i}Pr-DAB) (see 'Experimental') the complex Ru(CO)$_2$(PPh$_3$)(^{i}Pr-DAB) is probably not stable under the reaction conditions used and reacts to give Ru(CO)$_3$(PPh$_3$)$_2$ which was detected by both IR and ^{31}P NMR spectroscopy.

Supplementary material

Tables of the fractional coordinates of both the non-hydrogen and the hydrogen atoms of **6a**, anisotropic thermal parameters of the non-hydrogen atoms of **6a**, and full listings of bond lengths and bond angles of all atoms of **6a** (12 pages) can be ordered from the authors.

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